

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C08F 8/00, 8/42, 210/10 C08F 210/14 // (C08F 210/10 C08F 212/12) (C08F 210/14 C08F 212/12)	A1	(11) International Publication Number: WO 91/04992 (43) International Publication Date: 18 April 1991 (18.04.91)
(21) International Application Number: PCT/US89/05315 (22) International Filing Date: 22 November 1989 (22.11.89) (30) Priority data: 416,503 3 October 1989 (03.10.89) US 416,713 3 October 1989 (03.10.89) US (71) Applicant: EXXON CHEMICAL PATENTS INC. [US/ US]; 1900 E. Linden Avenue, Linden, NJ 07036 (US). (72) Inventors: POWERS, Kenneth, William ; 145 Robbins Ave- nue, Berkeley Heights, NJ 07922 (US). WANG, Hsien- Chang ; 14 Whittier Street, Edison, NJ 08820 (US). DI- AS, Anthony, Jay ; 932 Bachelor Avenue, Linden, NJ 07036 (US).	(74) Agent: COHEN, Harvey, L.; Exxon Chemical Company, P.O. Box 710, 1900 E. Linden Avenue, Linden, NJ 07036 (US). (81) Designated States: AT (European patent), AU, BE (Euro- pean patent), BR, CH (European patent), DE (European patent)*, ES (European patent), FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (Eu- ropean patent). Published <i>With international search report.</i>	
(54) Title: FUNCTIONALIZED COPOLYMERS OF PARA-ALKYLSTYRENE/ISOOLEFIN PREPARED BY NUCLEO- PHILIC SUBSTITUTION		
(57) Abstract A functionalized polymer of an isoolefin having about 4 to about 7 carbon atoms and a para-alkylstyrene, wherein at least one type of a functional group is attached to the para-alkyl group of the para-alkyl styrene, said polymer having a substantially homogeneous compositional distribution.		

DESIGNATIONS OF "DE"

Until further notice, any designation of "DE" in any international application whose international filing date is prior to October 3, 1990, shall have effect in the territory of the Federal Republic of Germany with the exception of the territory of the former German Democratic Republic.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MC	Monaco
AU	Australia	FI	Finland	MG	Madagascar
BB	Barbados	FR	France	ML	Mali
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GR	Greece	NL	Netherlands
BJ	Benin	HU	Hungary	NO	Norway
BR	Brazil	IT	Italy	PL	Poland
CA	Canada	JP	Japan	RO	Romania
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	LI	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
DE	Germany	LU	Luxembourg	TD	Chad
DK	Denmark			TG	Togo
				US	United States of America

- 1 -

FUNCTIONALIZED COPOLYMERS OF PARA-
ALKYLSTYRENE/ISOOLEFIN PREPARED BY NUCLEOPHILIC
SUBSTITUTION

FIELD OF THE INVENTION

The present invention relates to functionalized copolymers of an isoolefin and para-alkylstyrene. More particularly, the present invention relates to various functionalized copolymers of isobutylene and para-methylstyrene, and in particular such polymers ranging from tough, glassy polystyrene-like polymers to rubbery ozone-resistant polyisobutylene-like polymers. More particularly, the present invention relates to methods for producing functionalized copolymers of isobutylene and para-methylstyrene from halogenated copolymers of isobutylene and paramethylstyrene by a nucleophilic substitution reaction.

BACKGROUND OF THE INVENTION

The preparation and use of copolymers of styrene and isobutylene is known in the art. Thus, such copolymers ranging from tough, glassy high polystyrene content copolymers for use in plastic blends, to rubbery low styrene isobutylene copolymers for use as impact modifiers, etc., these copolymers have become well known in this art. Styrene and isobutylene have been copolymerized rather readily in the past under cationic polymerization conditions to yield these copolymers covering the entire compositional range. It is also known that blocky or random homogeneous copolymers can be produced by altering the copolymerization

- 2 -

conditions, such as shown in Powers, U.S. Patent No. 3,948,868. This patent thus describes the production of random homogeneous polymers comprising at least two cationically polymerizable monomers such as isobutylene and styrene. This disclosure also includes a lengthy list of various olefinic compounds including isobutylene, styrene, alpha-methylstyrene and other such compounds. Furthermore, these compounds have been used in a variety of applications, including use as adhesives in connection with other materials taking advantage of the surface characteristics of the polyisobutylene sequences, as coatings, as asphalt blends, and in various plastic blends. As is discussed in the '868 patent, it is also well known to produce terpolymers including isoprene, but doing so reduces the overall polymer molecular weight rendering the production of high molecular weight polymers therefrom difficult, and complicating the overall production sequence.

There have also been attempts to produce various functionalized polymers. For example, Hankey et al, U.S. Patent No. 3,145,187, discloses polymer blends which include a vinyl chloride polymer, a surfactant, and a chlorinated olefin polymer, and the latter is said by this patentee to include copolymers of various materials which can include isobutylene and styrene, as well as ring-alkyl styrenes, among a large number of other compounds, which olefin polymers can then be chlorinated by known methods.

The literature has also disclosed other routes for obtaining copolymers of isobutylene and

- 3 -

styrene, such as that shown in Powers et al., U.S. Patent No. 4,074,034, which discloses the copolymerization of isobutylene with halomethylstyrene. This technique requires the use of vinylbenzyl chloride and the like as a starting material, and utilizes a specified continuous solution process with solvent or mixed solvent systems in which the monomers are soluble under specified conditions. Aside from the need to employ the expensive vinylbenzyl chloride starting material, these processes also have limitations in terms of the quantity of aromatic chloromethyl functionality which can be incorporated in this manner without encountering excessive chain branching and gel formation during polymerization and polymer recovery because of the reactivity of the benzylic chlorine under cationic polymerization conditions. Such a procedure is also discussed by Jones, et al. "Isobutylene copolymers of vinylbenzyl chloride and isopropenylbenzyl chloride," Journal of Applied Polymer Science, Volume V, Issue No. 16, pp. 452-459 (1969) in which the aromatic monomer is said to be a mixture of the para and meta isomers.

There has also been some interest in the halomethylation of isobutylene/styrene copolymers, such as discussed in a paper by Sadykhov, et al. entitled "Chloromethylation of an isobutylene-styrene copolymer and some of its chemical reactions," Acerb. Neft. Khoz. 1979 (6) 37-9.

In an article by Harris, et al. entitled "Block and Graft Copolymers of Pivalolactone" Macromolecules, 1986, 19, 2903-2908, the authors

- 4 -

discuss the copolymerization of isobutylene with styrene and preferably a ring-methylated styrene. This article specifically discloses copolymerization with vinyl toluene, comprising a mixture of meta- and paramethylstyrene in approximately 65/35 amounts, and with para-methylstyrene, for the purpose of producing thermoplastic elastomer pivalolactone copolymer systems with no auto-oxidizable aliphatic unsaturation. The article fails to recognize any difference between the use of vinyl toluene and para-methylstyrene, and in any event, even when it employs the latter, it employs conditions which result in copolymers having the properties, including heterogeneous compositional distribution and very broad molecular weight distribution for the unfractionated copolymer, as set forth in Tables 4 and 5, which include an M_n for the unfractionated copolymer of 16,000, an M_w/M_n of 17.45 therefore, and a 4-methylstyrene content in the polymer which varies considerably from the monomer feed and varies significantly as a function of molecular weight.

Finally, there are also articles which discuss copolymers of isobutylene and paramethylstyrene without discussing any method for preparing them. These articles include Sadykhov, et al. "Studies of oxidative thermal degradation of copolymers of isobutylene with m- and p-methylstyrenes in a solution of mineral oils," and p-methylstyrenes in a solution of mineral oils," Uch. Zap. Azerb. Un. t. Ser. Khum. 1975 (304), 87-92, and other such articles. Furthermore, in Toman, et al. "Isobutylene Polymers and Copolymers

- 5 -

with Controlled Structure," App. 78/7, 339, (November 10, 1978), there is reference to the copolymerization of isobutylene with vinyl aromatic monomers. The search has thus continued for useful molecular weight copolymers of isobutylene and alkyl styrenes, and in particular for functionalized copolymers of this type which can be cross-linked, and otherwise used in a variety of applications.

Polymers with a saturated hydrocarbon backbone are well known to possess good environmental and aging resistance which makes them highly desirable in a variety of applications. Furthermore, rubbery copolymers containing major amounts of polyisobutylene are well known to possess low permeability, unique damping properties, and low surface energy which makes them particularly highly desired in many applications. However, the "inertness" of these saturated hydrocarbon polymers, their low reactivity and incompatibility with most other materials, and the difficulties in adhering them to, or using them in conjunction with most other materials has restricted their use in many areas.

We theorized that the introduction of controlled amounts of the desired specific functionality as pendant groups on the saturated hydrocarbon backbone would greatly extend usefulness by permitting these polymers to be adhered to other surfaces and/or be coreacted with or compatibilized with other functional polymers by "grafting" or cross linking reactions. We further theorized that the introduction of pendant functionality of the right type and amounts would permit these saturated

- 6 -

hydrocarbon polymers to be "painted" or coated with other materials or to be used as coatings on other materials and/or to be laminated with or dispersed in other materials to yield composite materials with a desired combination of properties.

As has already been pointed out, the fact that benzylic halogen functionality constitutes a very active electrophile that can be converted to many other functionalities via S_N nucleophilic substitution reactions has long been recognized and the chemical literature is replete with examples of these reactions. "Clean" conversions in high yield to many functionalities, including the following have been reported: aldehyde carboxy, amide, ether, ester, thioester, thioether, alkoxy, cyanomethyl, hydroxymethyl, thiomethyl, aminomethyl, cationic ionomers (quaternary ammonium or phosphonium, S-isothiuronium, or sulfonium salts), anionic ionomers (sulfonate and carboxylate salts), etc. In addition, the literature describes many examples in which a benzylic halogen is replaced by a cluster of other functionalities by nucleophilic substitution with a multifunctional nucleophile such as: tri-ethanol amine, ethylene polyamines, malonates, etc. Nearly all of this previous work has been with simple, small (i.e. non-polymeric) molecules containing the aromatic halomethyl (or benzylic) functionality. However, a considerable amount of art also exists on nucleophilic substitution reactions involving chloromethyl styrene and polystyrenes containing aromatic chloromethyl groups to introduce other functionalities. Much of this work involves reactions with "styragels" or lightly

- 7 -

cross-linked polystyrenes containing various amounts of benzylic chlorine, and while many of the same nucleophilic substitution reaction previously reported for small molecules containing benzylic chlorine have been achieved in "Styragels", it has been necessary to modify reaction conditions and in particular to often employ phase transfer catalysts in order to promote the desired substitution reaction. Reactions involving the benzylic chlorine in polystyrene have been more difficult to achieve than in simple small molecules because of the greater difficulty in achieving the intimate contact required between the reactants when one of the reactants (the aromatic chloromethyl moiety) is in a separate polymeric phase from the other reactant. Yields have also generally been lower and side reactions are more prevalent in the reactions involving the benzylic chlorine in polystyrene. However, since most of the work has been with "styragels", it has generally not been necessary to achieve high conversion in "clean" substitution reactions in order to preserve polymer solubility. Good recent reviews of this work involving chloromethyl styrene and "styragels" containing benzylic chlorines are in the literature (see Marcel Camps et al. in Chloromethylstyrene: Synthesis, Polymerization, Transformation, Applications in Rev. Macromol. Chem. Physics, C22(3), 343-407 (1982-83) and JMJ Frechet in Chemical Modification of Polymers via Phase Transfer Catalysts in "Crown Ethers and Phase Transfer Catalysts in Polymer Science", edited by Matthews and Canecher and Published by Plenum Press, NY, 1984, and Jean-Pierre Montheard, et al. in Chemical Transformations of Chloromethylated

- 8 -

Polystyrene in JMS- Rev. Macromol. Chem. Phys., C-28 (3&4) 503-592 (1988).

Previous workers have not applied nucleophilic substitution reactions to isobutylene/para-bromomethylstyrene/para-bromomethylstyrene para-methyl styrene terpolymers as we have done to produce the versatile, substantially saturated, pendant functionalized, soluble copolymers of this invention.

SUMMARY OF THE INVENTION

In accordance with the present invention applicants have discovered functionalized copolymers of an isoolefin having from 4 to 7 carbon atoms and a para-alkylstyrene wherein the functional groups of the copolymer are affixed to the paraalkyl group. In a preferred embodiment, the isoolefin comprises isobutylene, and the paraalkylstyrene comprises para-methylstyrene.

In accordance with another embodiment of the present invention, the functionalized copolymer consists essentially of a functionalized copolymer of an isoolefin having from 4 to 7 carbon atoms and a para-alkylstyrene; wherein the copolymer has a number average molecular weight (\bar{M}_n) of at least about 25,000, and preferably at least about 30,000. The functionalized copolymers also preferably have a ratio of weight average molecular weight (\bar{M}_w) to number average molecular weight, or \bar{M}_w/\bar{M}_n of less than about 6, more preferably less than about 4,

- 9 -

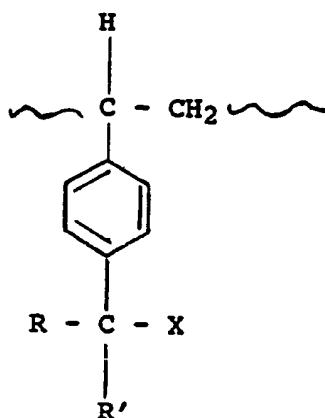
even more preferably less than about 2.5, and most preferably less than about 2.

In accordance with a preferred embodiment the preferred functionalized copolymers of the present invention are elastomeric functionalized copolymers, wherein these copolymers comprise between about 80 and 99.5 wt.% of the isooolefin such as isobutylene and between about 0.5 and 20 wt.% of the para-alkylstyrene such as para-methylstyrene. In accordance with another embodiment, however, where glassy or plastic materials are being produced as well, the functionalized copolymers comprise between about 10 and 99.5 wt.% of the isooolefin, or isobutylene, and between about 0.5 and 90 wt.% of the para-alkylstyrene, or para-methylstyrene.

In a further preferred embodiment the substantially homogeneous functionalized copolymers of the present invention have a number average molecular weight of from about 500 to about 25,000.

In accordance with a preferred embodiment of the copolymers of the present invention, these functionalized copolymers include the para-alkylstyrene having a functionalized group affixed to the alkyl group as

- 10 -



wherein R and R' are independently selected from hydrogen, alkyl, and the primary and secondary alkyl halides, and X is a functional group or functional groups selected from the group consisting of alkoxide, phenoxide, carboxylate, thiolates, thioethers, thiocarboxylates, dithiocarboxylates, thioureas, dithiocarbamates, xanthates, thio-cyanates, silanes, halosilanes, cyanides, organo lithium compounds, malonates, amides, amines, carbozoles, phthaleimide, pyridine, maleimide, phosphines, and cyanate and mixtures thereof. Preferably these functionalized copolymers are otherwise substantially free of any additional functional groups in the form of any ring functional groups or any functional groups on the polymer backbone chain (i.e., on the isoolefin carbons).

The copolymer of isoolefin having between 4 and 7 carbon atoms and the para-alkylstyrene is formed by admixing the isoolefin and the para-alkylstyrene in a copolymerization reactor under copolymerization conditions in the presence of a diluent, and a Lewis Acid catalyst, and maintaining

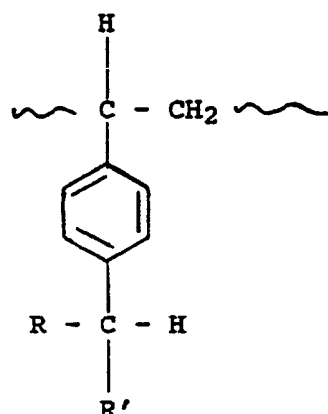
- 11 -

the copolymerization reactor substantially free of impurities which can complex with the catalyst or which can copolymerize with the isoolefin or the paraalkylstyrene. In this manner applicants have discovered that they are able to produce the above-described copolymers as direct reaction products, which, in their as-polymerized form, have a substantially homogeneous compositional distribution, and which can also consist essentially of isoolefin and paraalkylstyrene, and have a number average molecular weight of greater than about 25,000. The isobutylene/para-methylstyrene copolymer is insoluble in the preferred diluent, and the process is thus a slurry polymerization process. In another embodiment, however, in which the isobutylene/para-methylstyrene copolymer is soluble in the diluent, a solution polymerization process is described.

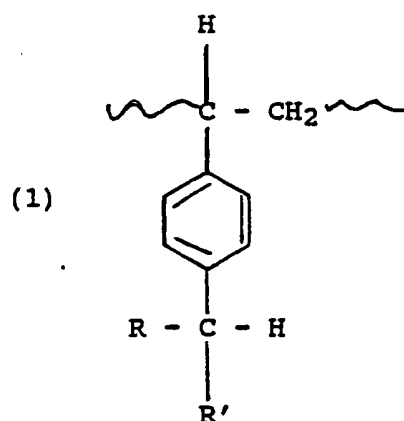
The isobutylene and para-methylstyrene [(throughout the remainder of this application the use of applicants' highly preferred embodiment of isobutylene and paramethylstyrene is intended to also include the potential use of various isoolefins and para-alkylstyrenes (as set forth above)] are present in the copolymer in amounts such that the isobutylene comprises between about 80 and 99.5% wt.% of the mixture and the para-methylstyrene comprises between about 0.5 and 20 wt.% of the mixture. In another embodiment, however, the isobutylene comprises from about 10 to 99.5 wt.% of the mixture and the para-methylstyrene comprises from about 0.5 to about 90 wt.% of the mixture. The copolymer of the isoolefin and the para-alkylstyrene is then partially selectively brominated for yield a

- 12 -

"base terpolymer" containing benzylic bromine functionality. The "base terpolymer" is produced by selective bromination of one of the benzylic hydrogens of the copolymer of an isoolefin having 4 to 7 carbon atoms and a para-alkylstyrene having the formula:

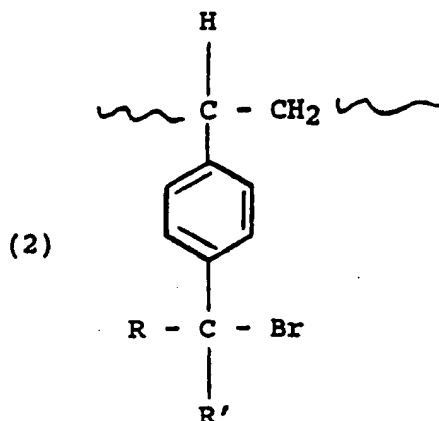


in the presence of bromine and a radical initiator so as to provide a brominated copolymer of isoolefin and para-alkylstyrene which copolymer includes the para-alkylstyrene as



- 13 -

or as

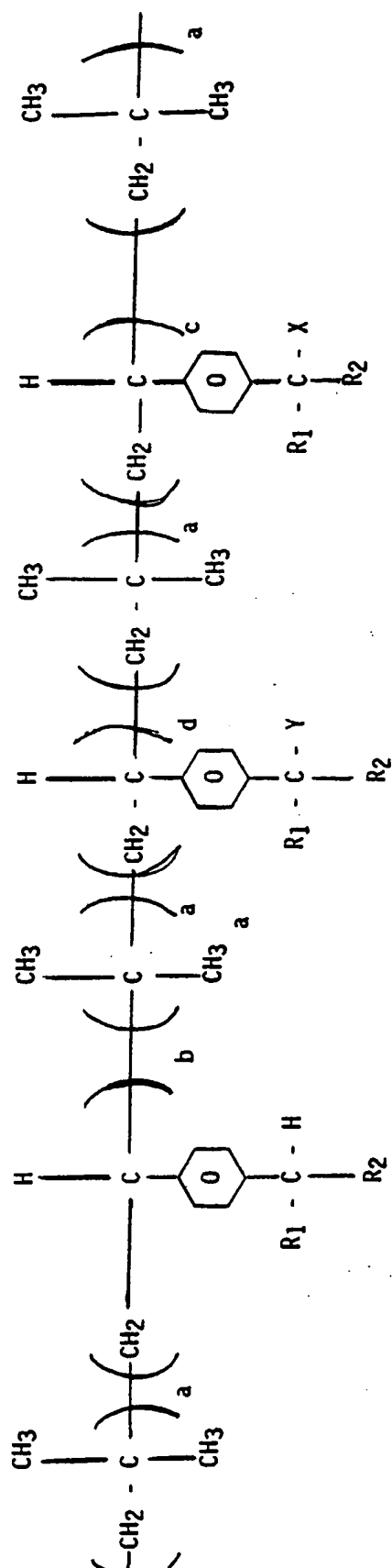


or as a mixture of (1) and (2), in which R and R' are independently hydrogen, alkyl, and the primary and secondary alkyl halides, and in which the copolymer is otherwise substantially free of ring bromine or any bromine on the polymer backbone chain. In accordance with one embodiment of the selected bromination process of the present invention, the radical initiator is light or heat. In accordance with another embodiment of the present invention, the radical initiator has a half-life of between about five and 2,500 minutes, and preferably comprises a bis azo compound.

Substitution of other functional groups for the benzylic bromine which is a very active and versatile electrophile can be accomplished by nucleophilic substitution reactions to introduce the desired functionality.

- 14 -

The pendant functionalized copolymers of the instant invention can be characterized by the formula:



- 16 -

wherein R_1 and R_2 are independently selected from the group consisting of hydrogen, alkyl, preferably C_1 to C_5 alkyl, and primary or secondary alkyl halides, preferably primary or secondary C_1 to C_5 alkyl halides, X is selected from the group consisting of chlorine and bromine, preferably bromine and Y represents a new functional group or functional groups attached to the polymer via nucleophilic substitution of one of the benzylic halogens.

BRIEF DESCRIPTION OF THE FIGURE

Figure 1 illustrates an NMR spectrum of linolenic acid.

Figure 2 illustrates an NMR spectrum of eleostearic acid.

Figure 3 illustrates a plot of time versus mole % for an acetate ester.

Figure 4 illustrates a plot of time versus mole % for hydroxy and ester formation.

DETAILED DESCRIPTION

This invention is initially based upon the discovery that the polymerization of these particular monomers under certain specific polymerization conditions now permits one to produce copolymers which comprise the direct reaction product (that is, in their as-polymerized form), and which have unexpectedly homogeneous uniform compositional

- 17 -

distributions. Thus, by utilizing the polymerization procedures set forth herein, the polymeric backbones of the novel functionalized copolymers of the present invention can be produced. These copolymers, as determined by gel permeation chromatography (GPC) demonstrate narrow molecular weight distributions and substantially homogeneous compositional distributions, or compositional uniformity over the entire range of compositions thereof. Put another way, at least about 95 wt. % of the copolymer product has a para-alkylstyrene content within about 10 wt.%, and preferably within about 7 wt.%, of the average para-alkylstyrene content for the overall composition, and preferably at least about 97 wt.% of the copolymer product has a para-alkylstyrene content within about 10 wt.%, and preferably within about 7 wt.%, of the average para-alkylstyrene content for the overall composition. In a most preferred embodiment hereof, this compositional uniformity is demonstrated by the fact that the normalized differential refractive index (DRI) and ultraviolet (UV) curves obtained by GPC for these copolymers are essentially superimposable on each other and substantially merge into a single curve in most instances. This substantially homogeneous compositional uniformity thus particularly relates to the intercompositional distribution. That is, with the novel copolymers of this invention, as between any selected molecular weight fraction the percentage of para-alkylstyrene therein, or the ratio of para-alkylstyrene to isooolefin, will be substantially the same, in the manner set forth above. Since the relative reactivity of para-alkylstyrene with an isooolefin such as

- 18 -

isobutylene is close to one, the intracompositional distribution of these copolymers will also be substantially random. That is, these copolymers are essentially random copolymers, and in any particular polymer chain the para-alkylstyrene and isooolefin units will be essentially randomly distributed throughout that chain.

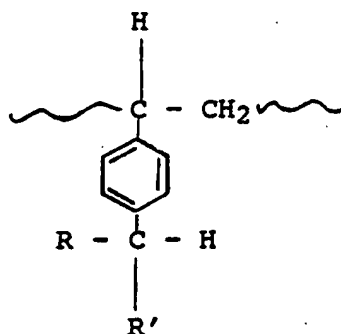
These properties of these copolymers lead to a number of distinct advantages over the prior art, including the ability to produce copolymers having high molecular weights, and in particular having number average molecular weights generally greater than about 25,000 preferably greater than about 50,000, and more preferably greater than about 100,000. These compositions also generally have viscosity average molecular weights greater than about 300,000, preferably greater than about 500,000, such as up to about 1,000,000 or more, or even up to about 2,000,000 or more.

In addition to these high molecular weight products, however, the copolymers of the present invention also include compositionally homogeneous copolymers having a relatively low number average molecular weight. These products also exhibit a relatively narrow molecular weight distribution, i.e., in both their high and low molecular weight forms. In particular, these copolymers thus exhibit $\overline{M}_w/\overline{M}_n$ values of less than about 6, preferably less than about 4, more preferably less than about 2.5, and most preferably less than about 2, and at the same time, depending upon the ultimate intended use thereof, can have low number average molecular

- 19 -

weight (M_n) from about 500 to about 25,000, preferably from about 750 to about 20,000, more preferably from about 1,000 to about 15,000, and most preferably from about 1,200 to about 10,000. The copolymers of the isooolefin and the para-alkylstyrene are disclosed in U.S. Serial No. 199,665, filed 5/22/88 which is hereby incorporated by reference.

The copolymers of the isooolefin and para-alkylstyrene are random and uniform and have narrow molecular weight distributions. Copolymers have also been produced at high molecular weights and can be made at low molecular weights as well. These random copolymers thus have uniformly distributed para-methylstyrene units distributed in all fractions of the copolymer, so that at least about 95 wt.% of the product has a para-methylstyrene content within about 10 wt.% of the overall average para-methylstyrene content. Thus, distributed throughout the copolymer are the para-methylstyrene units:



in which R and R' are, independently selected from the group consisting of hydrogen, alkyl, preferably

- 20 -

C₁ to C₅ alkyl, and primary or secondary alkyl halides, preferably primary or secondary C₁ to C₅ alkyl halides. These copolymers, as discussed above, have molecular weight distributions or M_w/M_n of less than about 6, preferably less than about 4, more preferably less than about 2.5, and most preferably less than about 2.

With respect to the ratio of the monomers employed to produce these copolymers of an isoolefin and a para-alkylstyrene it is a distinct advantage of the present invention that a very wide range of the ratio of the monomers in the copolymer product can be achieved in accordance with this invention. It is therefore possible for example to produce elastomeric copolymer products which include between about 80 and 99.5 wt.%, preferably between about 90 and 99 wt.%, more preferably between about 80 and 98.5 wt.%, and most preferably between about 80 and 98 wt.% of the isoolefin or isobutylene and between about 0.5 and 20 wt.%, preferably between about 1 and 20 wt.%, more preferably between about 1.5 and 20 wt.%, and most preferably between about 2 and 20 wt.% of the para-alkylstyrene, or preferably para-methylstyrene. On the other hand, it is also possible to produce thermoplastic materials comprising higher concentrations of para-alkylstyrene, and therefore the copolymers include between about 10 and 99.5 wt.%, preferably between about 10 and 99 wt.%, more preferably between about 10 and 98.5 wt.%, and most preferably between about 10 and 98 wt.% of the isoolefin or isobutylene, and between about 0.5 and 90 wt.%, preferably between about 1 and 90 wt.%, more preferably between about 1.5 and

- 21 -

90 wt.%, and most preferably between about 2 and 90 wt.% of the para-alkylstyrene, or preferably para-methylstyrene.

Isobutylene and para-methylstyrene are readily copolymerized under cationic conditions. The polymerization of the para-methylstyrene and isobutylene can be carried out by means of a Lewis Acid catalyst. Suitable Lewis Acid catalysts (including Friedel-Crafts catalysts) for the process according to the present invention thus include those which show good polymerization activity with a minimum tendency to promote alkylation transfer and side reactions which can lead to branching and the production of cross-links resulting in gel-containing polymers with inferior properties. The preferred catalysts are Lewis Acids based on metals from Group IIIa, IV and V of the Periodic Table of the Elements, including boron, aluminum, gallium, indium, titanium, zirconium, tin, vanadium, arsenic, antimony, and bismuth. The Group IIIa Lewis Acids have the general formula R_mMX_n , wherein M is a Group IIIa metal, R is a monovalent hydrocarbon radical selected from the group consisting of C_1 to C_{12} alkyl, aryl, alkylaryl, arylalkyl and cycloalkyl radicals; m is a number from 0 to 3; X is a halogen independently selected from the group consisting of fluorine, chlorine, bromine, and iodine; and the sum of m and n is equal to 3. Nonlimiting examples include aluminum chloride, aluminum bromide, boron trifluoride, boron trichloride, ethyl aluminum dichloride ($EtAlCl_2$), diethyl aluminum chloride (Et_2AlCl), ethyl aluminum sesquichloride ($Et_{1.5}AlCl_{1.5}$), trimethyl aluminum, and triethyl

- 22 -

aluminum. The Group IV Lewis Acids have the general formula MX_4 , wherein M is a Group IV metal and X is a ligand, preferably a halogen. Nonlimiting examples include titanium tetrachloride, zirconium tetrachloride, or tin tetrachloride. The Group V Lewis Acids have the general formula MX_y , wherein M is a Group V metal, X is a ligand, preferably a halogen, and y is an integer from 3 to 5. Non-limiting examples include vanadium tetrachloride and antimony pentafluoride.

The preferred Lewis Acid catalysts may be used singly or in combination with co-catalysts such as Bronsted Acids, such as anhydrous HF or HCl, or alkyl halides, such as benzyl chloride or tertiary butyl chloride. In particular, the most preferred catalysts are those which can be classified as the weaker alkylation catalysts, and these are thus the weaker Lewis Acids from among the catalysts set forth above. These most preferred catalysts, such as ethyl aluminum dichloride and preferably mixtures of ethyl aluminum dichloride with diethyl aluminum chloride, are not the catalysts that are normally preferred for use in conventional alkylation reactions, since again in the present case there is a strong desire to minimize side reactions, such as the indanyl ring formation which would be more likely to occur with those catalysts normally used to promote conventional alkylation reactions. The amount of such catalysts employed will depend on the desired molecular weight and the desired molecular weight distribution of the copolymer being produced, but will generally range from about 20 ppm to 1 wt.%, and preferably from about 0.001 to 0.2 wt.%,

- 23 -

based upon the total amount of monomer to be polymerized therein.

Suitable diluents for the monomers, catalyst components and polymeric reaction products include the general group of aliphatic and aromatic hydrocarbons, used singly or in admixture, and C₁ to C₆ halogenated hydrocarbons used in admixture with hydrocarbon diluents in an amount up to about 100% by volume of the total diluent fed to the reaction zone. Typically, when the monomers are soluble in the selected diluent the catalyst may not necessarily also be soluble therein.

The processes of the preparation of the copolymer of isoolefin and para-alkylstyrene can be carried out in the form of a slurry of polymer formed in the diluents employed, or as a homogeneous solution process. The use of a slurry process is, however, preferred, since in that case lower viscosity mixtures are produced in the reactor, and slurry concentrations of up to 40 wt.% of polymer are possible. At higher slurry concentrations it is possible to operate a more efficient process in which it is necessary to recycle less of the reactants and diluent for each unit of polymer produced. For instance, at 33% slurry concentration it is only necessary to recycle two units of unreacted reactants and diluent for each unit of polymer. In any event, the amount of diluent fed to the reaction zone should be sufficient to maintain the concentration of polymer in the effluent leaving the reaction zone below about 60 wt.%, and preferably between the range of about 5 and 35 wt.%, depending upon the

- 24 -

process being used and the molecular weight of polymer being produced. Too high a concentration of polymer is generally undesirable for several reasons, including poor temperature control, rapid reactor fouling, and the production of gel. Polymer concentrations which are too high will raise the viscosity in the reactor and require excessive power input to insure adequate mixing and the maintenance of effective heat transfer. Such inadequate mixing and loss of heat transfer efficiency can thus result in localized high monomer concentrations and hot spots in the reactor which can in turn cause fouling of reactor surfaces. Typical examples of the diluents which may be used alone or in admixture include propane, butane, pentane, cyclopentane, hexane, toluene, heptane, isooctane, etc., and various halohydrocarbon solvents which are particularly advantageous herein, including methylene chloride, chloroform, carbon tetrachloride, methyl chloride, with methyl chloride being particularly preferred.

It should also be noted that with any particular monomers (for example, isobutylene and paramethylstyrene), as the compositional distribution of the feed is altered there between, in order to maintain either a slurry or solution polymerization it can be necessary to change the diluents employed, depending upon the effect on the solubility of the copolymer in the diluent as the ratio of the monomers utilized therein is altered. An important element is the exclusion of impurities from the polymerization reactor, namely impurities which, if present, will result in complexing with

- 25 -

the catalyst or copolymerization with the isoolefins or the para-alkylstyrenes, which, in turn, will prevent one from producing the improved copolymer products of the present invention. Instead, products which do not have the substantially homogeneous compositional distributions and/or narrow molecular weight distributions of the present invention, will be produced. Most particularly, these impurities include the catalyst poisoning materials, moisture, and other copolymerizable monomers, such as, for example, meta-alkylstyrenes and the like. These impurities should be kept out of the system so that, in turn, the para-alkylstyrene is at least about 95.0 wt.% pure, preferably at least about 97.5 wt.% pure, most preferably at least about 99.5 wt.%, the isoolefin is at least about 99.5 wt.% pure, and preferably at least about 99.8 wt.% pure, and the diluents employed therein are at least about 99.0 wt.% pure, and preferably at least about 99.8 wt.% pure.

In general, the polymerization reactions for the manufacture of the copolymer of isoolefin and para-alkylstyrene of the present invention are carried out by admixing the para-methylstyrene and isobutylene in the presence of the catalyst (such as a Lewis Acid catalyst) and diluent in a copolymerization reactor), with thorough mixing, and under copolymerization conditions, including temperatures of at least less than about 0°C, in the case of lower molecular weight polymers, and providing a means of removing the heat of polymerization in order to maintain a desired reactor temperature. In particular, the polymerization may be carried out

- 26 -

under batch conditions of cationic polymerization, such as in an inert gas atmosphere and the substantial absence of moisture. Preferably the polymerization is carried out continuously in a typical continuous polymerization process using a baffled tank-type reactor fitted with an efficient agitation means, such as a turbo-mixer or propeller, and draft-tube, external cooling jacket and internal cooling coils or other means of removing the heat of polymerization, inlet pipes for monomers, catalysts and diluents, temperature sensing means and an effluent overflow to a holding drum or quench tank. The reactor must be purged of air and moisture and charged with dry, purified solvent or a mixture of solvents prior to introducing monomers and catalyst.

Reactors which are typically used in butyl rubber polymerizations are generally suitable for use in the polymerization reactions of the present invention. These reactors are basically large heat exchangers in which the reactor contents are rapidly circulated through rows of heat exchange tubes which are surrounded by boiling ethylene so as to remove the heat of polymerization, and then through a central draft tube by means of an efficient marine-type impeller. Catalyst and monomers are introduced continuously into the reactor and mixed by the pump, and reactor effluent then overflows into a steam-heated flash tank. Heat of polymerization can also be removed by a pump-around loop in which the reactor contents are continuously circulated through an external heat exchanger in such a pump-around loop.

- 27 -

When conducting a slurry polymerization process the reactor is generally maintained at temperatures of between about -85°C and -115°C , and preferably between about -89°C and -96°C . Solution polymerizations and cement suspension polymerizations can be run at much warmer temperatures, such as about -40°C , depending on the copolymer molecular weight desired and the particular catalyst system used. Therefore, an acceptable solution polymerization temperature range is about -35°C to about -100°C , and preferably about -40°C to about -80°C .

The overall residence time can vary, depending upon, e.g., catalyst activity and concentration, monomer concentration, reaction temperature, and desired molecular weight, and generally will be between about one minute and five hours, and preferably between about 10 and 60 minutes.

Since the reactor does gradually foul with polymer in the slurry polymerization process, however, it does generally become necessary to periodically remove the reactor from production for cleaning. It is thus most important that the fouling polymer be soluble, so that the reactor can be cleaned by solvent washing and then returned to service. Any deposition of insoluble "gel" polymer in the reactor would be unacceptable, since it would render solvent washing ineffective, and necessitate the use of elaborate and expensive reactor cleaning procedures. This necessity to avoid the deposition of a polymer "gel" in the reactor is one of the limitations on the amount of diene which can be used

- 28 -

in making butyl rubbers, (e.g., isobutylene-isoprene copolymer).

The para-methylstyrene/isobutylene copolymers of this invention also afford significant advantages when produced using a solution polymerization process. Since para-methylstyrene does not cause the severe molecular weight depression characteristic of dienes, and since the molecular weight vs. polymerization temperature response of these copolymers is much flatter than with diene functional butyl copolymers, high molecular weight copolymers can be made at much warmer temperatures (i.e., about -40°C vs. less than about -90°C with the diene functional butyl copolymers). These warmer polymerization temperatures translate into a much lower viscosity at any given polymer concentration and molecular weight. In particular, it is now possible to conduct these solution polymerizations at temperatures of from about -35°C to about -100°C , and preferably from about -40°C to about -80°C . When producing the low molecular weight polymers of this invention, for example, M_n of less than 25,000, temperatures as warm as 0°C can be used, or even up to about $+10^{\circ}\text{C}$ for very low molecular weight polymers with M_n in the range of about 500 to 1,000 M_n . Furthermore, the para-methylstyrene/isobutylene copolymers have a much narrower molecular weight distribution than do the diene functional butyl rubbers, and this also results in a much lower solution viscosity at a given number average molecular weight.

- 29 -

Solution polymerization has the further advantage, particularly with the para-methylstyrene/isobutylene copolymers, in that the copolymers are produced in a desirable solution state to permit post polymerization chemical modification, as pointed out above, (e.g., halogenated). It is also possible to perform these post-polymerization reactions on polymer in the bulk state (i.e., using an internal mixer, extruder, etc.), but many reactions can be more easily performed in a more controlled manner on polymer solutions, which afford better mixing, heat transfer, removal of unwanted by-products, etc.

The polymerization processes can also be carried out in the form of a so-called "cement suspension" polymerization process. In particular, these are polymerization reactions carried out in a selected diluent such that the polymer is only slightly soluble in the diluent, and the diluent is sufficiently soluble in the polymer so that a second liquid phase is formed which contains substantially all of the polymer, but wherein the continuous phase or diluent phase has a sufficiently low viscosity so that the second or polymer-rich liquid phase can be dispersed therein. In one form of these cement suspension polymerizations they are carried out in such a diluent whose lower critical solution temperature for the polymer to be prepared is below the temperature at which the reaction is to be carried out. The lower critical solution temperature, in turn, is defined as the temperature above which the polymer is no longer soluble in a solvent. In addition, in accordance with these processes, it

- 30 -

would be appreciated that as the temperature of a solution of polymer and diluent is increased, a temperature will be reached above which the polymer is no longer soluble. If maintained at this temperature, separation of two phases will occur with generally the lower portion being a heavier polymer-rich phase and the upper portion being a lighter solvent-rich phase. This phenomenon can thus be utilized to separate polymers from solution in conventional solution polymerization processes as discussed above. In any event, to achieve the desirable two-phase "cement suspension" it is necessary that the light phase be a very poor solvent for the polymer to maintain low viscosity, and that the polymer-rich heavy phase separate out and contain enough solvent so it behaves as a liquid and can be dispersed in the light phase. The particular details of such cement suspension processes are set forth in U.S. Patent No. 3,932,371, and the description of same is incorporated herein by reference thereto.

An example of a post-polymerization chemical modification reaction that can be run on bulk recovered polymer, and can also be run on polymer solution produced in a solution polymerization process (after suitable quenching and removal of residual monomers) is halogenation (e.g., radical bromination) to produce the very versatile benzylic halogen-functional copolymers described herein. The surprising ease and highly selective nature of radical halogenation to introduce a benzylic halogen, and the great versatility of the benzylic

- 31 -

halogen, makes this a most preferred modification reaction.

Functionality introducing reactions such as halogenation are carried out on the para-methylstyrene/isobutylene copolymers produced by any of the above polymerization methods in a separate post-polymerization step, with direct halogenation, and most preferably radical halogenation, being the preferred reaction. It is generally desirable to treat the polymerization copolymer product in an appropriate manner, prior to such halogenation, in order to quench the catalyst and/or remove catalyst residues, remove residual unconverted monomers, and put it into a convenient form for the halogenation reaction.

It is nearly always desirable to quench the catalyst in the reactor effluent in order to prevent continued polymerization, with the concomitant production of low molecular weight ends and/or to prevent degradation and cross-linking reactions from occurring as the effluent is warmed. This quenching can be accomplished in a conventional manner. Generally speaking, with the aluminum-based catalysts usually employed in making the copolymers and with the high catalyst efficiencies achieved, a separate catalyst residue removal step is not required, but much of this residue is extracted into the water phase in conjunction with conventional water-based finishing processes anyway.

Residual unconverted monomers left in the copolymer will react during halogenation to both

- 32 -

consume halogen and produce generally undesirable by-products, and their presence thus renders it difficult to control and measure the amount of desired functionality introduced into the copolymer. Hence, except in cases where the copolymer has been polymerized at very high conversion, it is usually necessary to remove these residual monomers. Unreacted isobutylene is volatile enough to be easily removed in any of a variety of stripping operations, but para-methylstyrene, with its high boiling point of 170°C, is much more difficult to remove. It is therefore advantageous to polymerize at very high para-methylstyrene conversion levels so that its removal and/or recycle becomes unnecessary or, at least involves smaller amounts of material.

The halogenation reaction itself can be carried out in the bulk phase or on copolymer either in solution or in a finely dispersed slurry. Bulk halogenation can be effected in an extruder, or other internal mixer, suitably modified to provide adequate mixing and for handling the halogen and corrosive by-products of the reaction. It has the advantages of permitting complete removal of residual unreacted para-methylstyrene by conventional finishing operations prior to halogenation, and of avoiding possible diluent halogenation as an undesired side reaction. It has the disadvantages of requiring a much more expensive and high powered reactor (i.e., extruder) than is required for solution halogenation, and of providing poorer mixing, thermal control, etc., than can be achieved in solution, so that the halogenation reaction is conducted under less homogeneous, more difficult to

- 33 -

control conditions. The details of such bulk halogenation processes are set forth in U.S. Patent No. 4,548, 995, which is incorporated herein by reference thereto.

Solution halogenation is advantageous in that it permits good mixing and control of halogenation conditions to be achieved, easier removal of undesired halogenation by-products, and a wider range of initiators of halogenation to be employed. Its disadvantages include the need for removal of residual unreacted para-methylstyrene prior to halogenation, the presence of complicating side reactions involving solvent halogenation, and a solution step if a non-solution polymerization process is used to prepare the copolymer, as well as removal, clean-up and recycle of the solvent. Suitable solvents for such halogenation include the low boiling hydrocarbons (C₄ to C₇) and halogenated hydrocarbons. The halogenation can also be conducted with the copolymer as a fine slurry or cement suspension in a suitable diluent which is a poor solvent for the copolymer. This is advantageous from a viscosity viewpoint and allows high solids content during halogenation, but it does require that the slurry or suspension be stable with little tendency to agglomerate or plate out on reactor surfaces. Since the high boiling point of para-methylstyrene makes its removal by conventional distillation impractical, and since it is difficult to completely avoid solvent halogenation, it is very important where solution or slurry halogenation is to be used that the diluent and halogenation conditions be chosen to avoid diluent halogenation, and

- 34 -

that residual para-methylstyrene has been reduced to an acceptable level.

Halogenation of the para-methylstyrene isobutylene copolymers of this invention is significantly different from halogenation of isobutylene-isoprene (butyl) rubbers because the primary reactive site for halogenation is entirely different. The para-methylstyrene/isobutylene copolymers contain no in-chain (backbone) olefinic unsaturation contribution from the para-methylstyrene, and the primary reactive halogenation site is thus the enchaind para-methylstyrene moiety, which is far less reactive than the olefinic site in butyl rubber. Furthermore, since the broad range of copolymer compositions of the present invention can include para-methylstyrene contents of greater than 20% and up to about 90%, the potential for such reactive sites is clearly increased. Under typical butyl rubber halogenation conditions, however (e.g., dark, non-catalyzed reactions, in a hydrocarbon solvent, at low temperature (such as less than about +80°C) and for short contact times (such as less than about 10 minutes)) no detectable halogenation of the para-methylstyrene copolymer even occurs. Furthermore, while it is possible to chlorinate para-methylstyrene copolymers in a polar diluent, the chlorinated species produced are entirely different than in the case of isobutylene-isoprene (butyl) rubber. Such chlorinated species of the present invention include chlorine on the aromatic ring, and on the polymer backbone, as well as the preferred primary benzylic chlorination, in contrast

- 35 -

to the chlorination of the olefinic sites in the prior art copolymers.

With halogenation of para-methylstyrene/isobutylene copolymers, it is possible to halogenate the ring carbons, but the products are rather inert and of little interest. It has surprisingly been found, however, that it is possible to introduce this desired benzylic functionality into the para-methylstyrene/isobutylene copolymers hereof in high yields and under practical conditions without obtaining excessive polymer breakdown, cross-linking or other undesirable side reactions.

When halogenation of the para-methylstyrene/isobutylene copolymers hereof is carried out without using the specified selected reaction conditions, catalysts, reagents and initiators hereof, it tends to either not occur at all, or to proceed by various routes, so as to produce a variety of halogenated products. Thus, if chlorine or bromine is added to a solution of para-methylstyrene/isobutylene copolymer in a low dielectric constant hydrocarbon solvent, such as hexane or cyclohexane, in the dark at 30-60°C for about five minutes, essentially no reaction occurs. On the other hand, if the chlorination reaction is run in a more polar (higher dielectric constant) diluent, such as methylene chloride, then chlorination does occur, but apparently by many different routes, so that a variety of different chlorinated products are produced thereby. These include some of the highly desirable primary benzylic chlorine resulting from

- 36 -

substitution on the ring methyl group, but a major amount of less desirable chlorinated products.

It is known in connection with the halogenation of small molecules that the side chain halogenation of alkyl-substituted benzenes, as opposed to nuclear substitution, is favored by radical instead of ionic conditions. This might therefore be said to suggest that such radical conditions, including the avoidance of Friedel-Crafts catalysts (or metallic halogenation catalysts in general), the avoidance of polar diluents, and the use of photochemical, thermal, or other radical initiators, would be preferred for the selective halogenation of the copolymers hereof. However, it is also known that the halogenation of polymers does not necessarily follow the same routes as that of these small molecules, particularly since even minor side reactions can be extremely significant. Furthermore, it is known that, in radical halogenation, with concurrent hydrogen replacement, tertiary hydrogens are more easily replaced than are secondary hydrogens, which are more easily replaced than are primary hydrogens. Therefore, it might be expected that the tertiary benzylic hydrogens of the polymer backbone would be more easily replaced than the primary benzylic hydrogens on the enchaind para-methylstyryl moiety in the copolymers hereof.

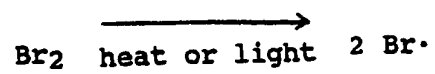
It has rather surprisingly been found, however, that radical bromination of the enchaind para-methylstyryl moiety in the copolymers of this invention can be made highly specific with almost exclusive substitution occurring on the para-methyl

- 37 -

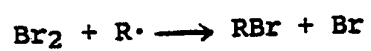
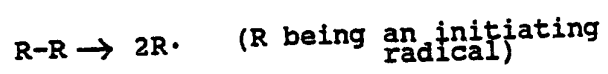
group, to yield the desired benzylic bromine functionality. The high specificity of the bromination reaction can thus be maintained over a broad range of reaction conditions, provided, however, that factors which would promote the ionic reaction route are avoided (i.e., polar diluents, Friedel-Crafts catalysts, etc.).

Thus, solutions of the para-methylstyrene/isobutylene copolymers in hydrocarbon solvents such as pentane, hexane or heptane can be selectively radically brominated on the para-methyl position using light, heat, or selected radical initiators (according to conditions, i.e., a particular radical initiator must be selected which has an appropriate half-life for the particular temperature conditions being utilized, with generally longer half-lives preferred at warmer hydrogenation temperatures) as promoters of radical halogenation, to yield almost exclusively the desired benzylic bromine functionality, via substitution on the para-methyl group, and without appreciable chain scission and/or cross-linking. Without wishing to be bound by any theory, it is believed that the bromination reaction proceeds by means of a rapid radical chain reaction with the chain carrier being, alternatively, a bromine atom and a benzylic radical resulting from hydrogen atom abstraction from a para-methyl group on the enchaind para-methylstyryl moiety. The proposed mechanism thus involves the following steps:

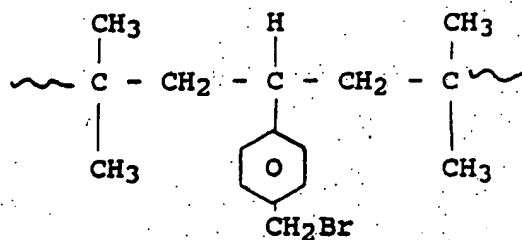
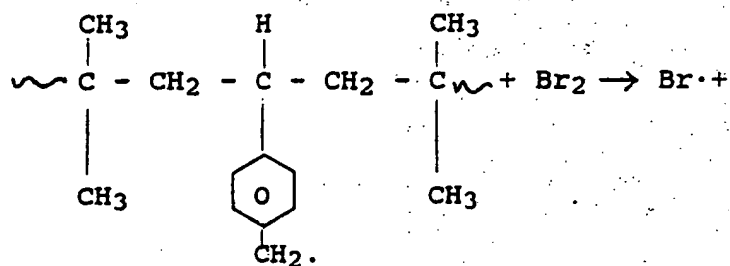
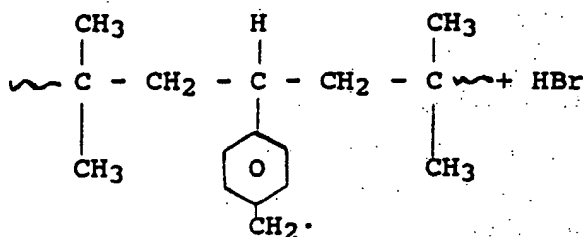
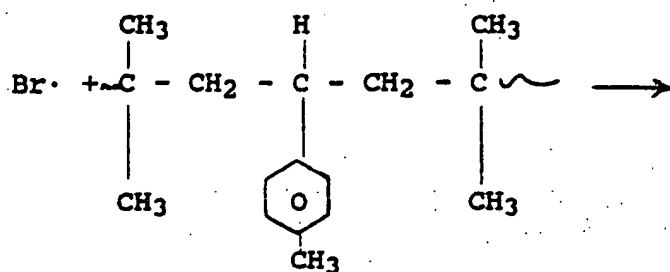
- 38 -

1. Initiation

or



- 39 -

2. Chain Reaction

The reaction terminates when one of the radicals reacts with some radical trap in the

- 40 -

system, or the radicals destroy themselves by recombination or disproportionation.

This reaction can be initiated as shown in step (1) above by formation of a bromine atoms, either photochemically or thermally (with or without the use of sensitizers), or the radical initiator used can be one which preferentially reacts with a bromine molecule rather than one which reacts indiscriminately with bromine atoms, or with the solvent or polymer (i.e., via hydrogen abstraction). The sensitizers referred to are those photochemical sensitizers which will themselves absorb lower energy photons and disassociate, thus causing, in turn, disassociation of the bromine, including materials such as iodine. It is thus preferred to utilize an initiator which has a half life of between about 0.5 and 2500 minutes under the desired reaction conditions, more preferably about 10 to 300 minutes. The amount of initiator employed will usually vary between 0.02 and 1% by weight on the copolymer, preferably between about 0.02 and 0.3%. The preferred initiators are bis azo compounds, such as azobisisobutyronitrile, azobis (2,4-dimethylvalero) nitrile, azobis (2 methylbutyro) nitrile, and the like. Other radical initiators can also be used, but it is preferred to use a radical initiator which is relatively poor at hydrogen abstraction, so that it reacts preferentially with the bromine molecules to form bromine atoms rather than with the copolymer or solvent to form alkyl radicals. In those cases, there would then tend to be resultant copolymer molecular weight loss, and promotion of undesirable side reactions, such as cross-linking.

- 41 -

The radical bromination reaction of this invention is highly selective, and almost exclusively produces the desired benzylic bromine functionality. Indeed, the only major side reaction which appears to occur is disubstitution at the para-methyl group, to yield the dibromo derivative, but even this does not occur until more than about 60% of the enchaind para-methylstyryl moieties have been monosubstituted. Hence, any desired amount of benzylic bromine functionality in the monobromo form can be introduced into the copolymers of this invention, up to about 60 mole % of the para-methylstyrene content. Furthermore, since the para-methylstyrene content can be varied over a wide range as described herein, it is possible to therefore introduce a significant functionality range. The halogenated copolymers of this invention are thus highly useful in subsequent reactions, for example cross-linking reactions.

It is desirable that the termination reactions discussed above be minimized during bromination, so that long, rapid radical chain reactions occur, and so that many benzylic bromines are introduced for each initiation, with a minimum of the side reactions resulting from termination. Hence, system purity is important, and steady-state radical concentrations must be kept low enough to avoid extensive recombination and possible cross-linking. The reaction must also be quenched once the bromine is consumed, so that continued radical production with resultant secondary reactions (in the absence of bromine) do not then occur. Quenching may be accomplished by cooling, turning off the

- 42 -

light source, adding dilute caustic, the addition of a radical trap, or combinations thereof.

Since one mole of HBr is produced for each mole of bromine reacted with or substituted on the enchaind para-methylstyryl moiety, it is also desirable to neutralize or otherwise remove this HBr during the reaction, or at least during polymer recovery in order to prevent it from becoming involved in or catalyzing undesirable side reactions. Such neutralization and removal can be accomplished with a post-reaction caustic wash, generally using a molar excess of caustic on the HBr. Alternatively, neutralization can be accomplished by having a particulate base (which is relatively non-reactive with bromine) such as calcium carbonate powder present in dispersed form during the bromination reaction to absorb the HBr as it is produced. Removal of the HBr can also be accomplished by stripping with an inert gas (e.g., N₂) preferably at elevated temperatures.

The brominated, quenched, and neutralized para-methylstyrene/isobutylene copolymers can be recovered and finished using conventional means with appropriate stabilizers being added to yield highly desirable and versatile functional saturated copolymers which are useful in many reactions and applications.

In particular, since little if any tertiary benzylic bromine is produced in the copolymer molecule, the potential dehydrohalogenation reaction will be almost entirely eliminated therein. This

- 43 -

results in a halogenated polymer of improved stability. In addition, presence of the bromine on the ring-methyl group leads to several additional significant advantages with respect to this product. It permits functionalization by substitution of other functional groups at that site.

The benzylic bromine (halogen) functionality is uniquely suited as the base from which the versatile functionalized saturated copolymers of this invention can be made because it can be made to undergo "clean" nucleophilic substitution reactions with a great range of nucleophiles, so that almost any desired type and amount of functionality can be introduced without undesirable side reactions and under conditions which are mild enough to avoid degradation and/or cross linking of the saturated copolymer backbone containing the pendant benzylic halogen functionality. Furthermore, in many instances, it is possible to only partially convert the pendant benzylic halogen to another desired functionality while retaining some, or to later convert another portion of the remaining benzylic halogen functionality to yet another new functionality, so that copolymers containing mixed functionalities can be made. The mixed functionality can advantageously provide unique combinations of properties, such as grafting with another functional polymer via one of the functionalities and then cross-linking or adhering to some surface via another of the functionalities.

One of the attributes of the benzylic halogen functionality of the radically halogenated

- 44 -

isobutylene/paramethylstyrene copolymers which makes them an "ideal" base copolymer from which to prepare the various functionalized saturated copolymers of this invention is the wide range of nucleophilic substitution reactions this benzylic halogen functionality will undergo and the relatively mild conditions under which these nucleophilic substitution reactions will proceed. A benzylic halogen functionality constitutes a very active electrophile which will react under suitable conditions with any nucleophile capable of donating electrons to it. Suitable nucleophiles include those containing oxygen, sulfur, nitrogen, phosphorus, carbon, silicon, and various metals including especially magnesium, lithium, sodium, and potassium. Equally important to this versatility in types of nucleophiles which will react with the benzylic halogen functionality is the relatively mild conditions under which these nucleophilic substitution reactions proceed so that substitution reactions can be completed to introduce the desired new functionality without cleavage or cross-linking reactions involving the saturated hydrocarbon backbone of the isobutylene/paramethylstyrene copolymer.

Another of the attributes of the benzylic halogen functionality is the "cleanness" with which the desired substitution reactions can be made to proceed without undesirable side reactions. The benzylic halogen functionality will undergo clean substitution reactions without complicating elimination reactions. This attribute is extremely important in reactions involving soluble high polymers, since even a tiny amount of a side

- 45 -

reaction which can lead to coupling may lead to gelation. In reactions involving simple molecules (which are usually mono-functional) yields of only 70% of the desired product may be acceptable, since purification and separation of the undesired products is relatively simple. In reactions involving already cross-linked polymers (i.e. "styragels") lower yields to the desired product may also be acceptable, since the starting polymer is already insoluble. However, in reactions with the soluble high polymers of this invention which contain many functional groups per molecule, it is necessary to achieve >99% of the desired substitution reaction in order to maintain solubility during reaction and recovery. Tiny, almost insignificant (in other reactions) amounts of side reactions which yield coupling which produces "gel" and may interfere with usefulness. Furthermore, purification of the substituted polymer to remove unwanted side products is usually very difficult or impossible. Hence, the importance of the "clean" single route to high yield nucleophilic substitution reactions which is achievable with benzylic halogen functionality under controlled conditions. By using isobutylene/para-methylstyrene/para-bromomethylstyrene terpolymers as a "base" polymer for modification, and by conducting nucleophilic substitution reactions under appropriate and controlled conditions, soluble backbone saturated, copolymers containing useful pendant functionality have been prepared: Examples include:

1. Esters (many containing other functional groups such as acetate, stearate,

- 46 -

linoleate, eleostearate, acrylate, cinnamate, etc.

2. Hydroxyl (attached directly in place of the benzylic bromine or attached via another linkage.
3. Carboxy
4. Nitrile
5. Quaternary Ammonium salts
6. Quaternary Phosphonium salts
7. S-isothiuronium salts
8. Dithiocarbamate esters
9. Mercaptans

While every possible derivative that could be prepared by nucleophilic substitution reactions on the isobutylene/para-methylstyrene/para-bromomethylstyrene terpolymers has not been prepared, it is obvious that one skilled in the art could attach almost any desired pendant functionality and many mixtures of functionalites as desired for various applications by applying the principles disclosed in this invention.

The "key" requirements for producing the versatile, pendant functionalized, backbone saturated, soluble copolymers of this invention via "clean" nucleophilic substitution reactions are:

1. Use of the isobutylene/para-halomethylstyrene/paramethylhalogenated paramethylstyrene "base" terpolymers for nucleophilic substitutions under appropriate, controlled conditions. The composition of the terpolymer can be varied as desired to

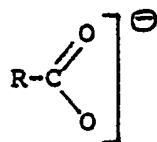
- 47 -

yield the desired combination of properties (i.e. Tg, hardness, flexibility, impact strength, functionality level, etc.).

2. Choosing the nucleophile and reaction medium so as to achieve the required intimate contact between the benzylic halogen attached to the base terpolymer and the nucleophile. It should be recognized that in some instances this can be accomplished by using a different solvent or reaction medium for the polymer and for the nucleophile and then employing an appropriate phase transfer catalyst to promote the reaction.
3. Achieving specific solvation at the reaction site so that the desired nucleophilic substitution reaction is facilitated at mild conditions.
4. Avoiding "vigorous" or "harsh" reactants or reaction conditions such as strong "hard" bases or high temperatures that would cause a loss in reaction specificity and allow side reactions to become important and/or cause cross-linking or degradation reactions to occur.
5. Choosing the nucleophilic reagent and promoters appropriately so that the desired substitution reaction occurs

- 48 -

quickly under mild conditions and potential undesired side reactions are avoided. For example: In using an



nucleophile in an

esterification reaction to replace the benzylic bromines on an isobutylene/para-bromomethylstyrene "base" terpolymer, one could chose the potassium salt of the acid as the nucleophilic reagent, along with 18 Crown-6 to solvate the potassium ion and promote the desired esterification substitution reaction, or one could choose the tetrabutyl ammonium counter ion in an appropriate solvent as a nice "soft" acid to promote the reaction rather than trying to use a "hard" ionic salt of the carboxylic acid as the nucleophilic reagent.

6. Choosing reaction conditions to minimize sequential reactions by recognizing that the nucleophilic substitution reaction being conducted can itself form attached pendant nucleophilic reagents on the base copolymer backbone and that these already attached nucleophilic reagents can nucleophilically "attack" other unreacted benzylic bromines on the base terpolymer in a sequential manner to consume the desired already attached new functionality and at the same time produce undesirable cross-linking of gelation.

- 49 -

Thus reaction conditions must be chosen such that the unreacted nucleophilic reagent being used in the nucleophilic substitution reaction being conducted is either a much stronger more reactive nucleophile or is present in great excess over any attached nucleophilic reagent being formed in the substitution reaction. Thus, in attempting to replace the benzylic bromines of the base terpolymer of this invention with mercaptan groups, it must be recognized that the attached SH groups will form attached mercaptide nucleophilic reagents under basic conditions and these attached mercaptide groups will react with other benzylic bromines to consume the already attached pendant mercaptan functionality and produce undesired thioether cross-links resulting in "gelled" polymer instead of the desired pendant functionalized polymer of the invention.

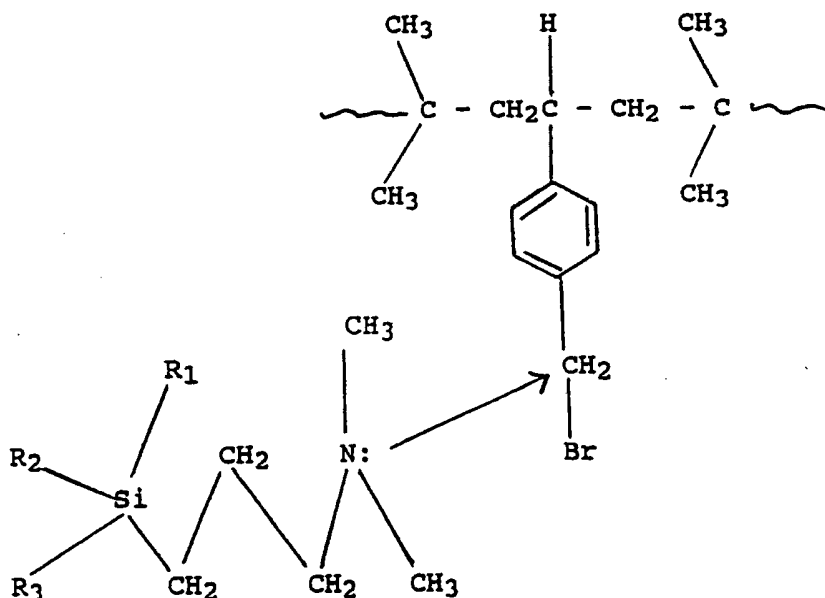
Likewise, in producing a pendant hydroxy functionalized polymer of this invention, it must be recognized that the attached-OH groups will form alkoxide nucleophilic reagents under strongly basic conditions and these attached alkoxide groups can react in a sequential manner with other unreacted benzylic bromines of the base terpolymer to consume the already attached pendant hydroxy functionality to produce ether cross links resulting in "gelled" polymer rather than the desired pendant functionalized polymer of this invention.

This "key" requirement of recognizing the potential for sequential reactions and choosing conditions to minimize them is especially important

- 50 -

in cases where it is desired to produce the pendant functionalized saturated polymers of this invention with mixed pendant functionality. In these mixed functionality polymers, it is extremely important to choose functionalities and conditions such that the desired pendant functionalities are preserved and sequential reactions are avoided.

The polymers of isoolefin and para-alkylstyrene - silane derivatized polymers represent another broadly useful family of materials which can be easily prepared by nucleophilic displacement through the use of suitable nucleophilic silane reagents like (N,N-Dimethyl-3-aminopropyl) silanes, as depicted below.



- 51 -

Wherein R_1 , R_2 and R_3 are each independently selected from the group consisting of: H, Cl, and O-(alkyl) wherein the alkyl group has about 1 to about 5 carbon atoms such as methyl, ethyl, etc.

The reactivity of these derivatives can be varied based upon the number and type of silane species present.

The polymers of isooolefin and para-alkylstyrene containing Si-Cl bonds are the most reactive toward a variety of nucleophiles, including as weak a nucleophile as water. Thus these materials are vulcanizable by exposure to the atmosphere and are therefore very useful as room temperature vulconizable compositions (RTVs).

Likewise these polymers containing Si-O(alkyl) bonds are also reactive with a variety of nucleophiles (though not as reactive as Si-Cl) which also include water. Again this reactivity can be exploited in RTV applications, especially where the emission of neutral species during curing is preferred.

Uniquely reactive are the polymers of isooolefin and paraalkylstyrene - silane derivatives which contain Si-H bonds. They undergo three fundamental types of reactions. They can react with hydroxyl or silanol functionalized materials in the presence of tin octoate, zinc octoate and other metal salts to form bonds with the evolution of hydrogen. This reaction can be used to impart

- 52 -

hydrophobicity to glass, leather, paper or fabric surfaces.

The Si-H functionality will react with olefins in the presence of certain free radical or precious metal catalysts. This reaction opens the opportunity for addition cure (RTV) or low temperature vulcanization. Mixtures of these polymers with another olefin containing polymer like polybutadiene or vinyl functional silicones will rapidly yield a intermolecular crosslinked system of the polymers of isoolefin and paraalkylstyrene and the other polymer. The polymers of isoolefin and paraalkylstyrene - vinyl silicone system will provide a useful thermally stable crosslink system which exhibits improved permeability properties over existing silicone systems.

The third useful reaction for these Si-H polymers of isoolefin and paraalkylstyrene derivatives is as polymeric reducing agents. SiH compounds are known to be active mild selective reducing agents for nitroaromatics, acid chlorides, aldehydes and ketones. Binding these reagents to polymers offers the advantage of ease of separation; the polymer is easy to remove from the low molecular weight reduced species and no hydrolysis of the remaining reagent is necessary prior to isolation. Another advantage is that these reductions can be run in the presence of air and moisture in a wide range of solvent systems including hexane, methylene chloride and dioxane.

- 53 -

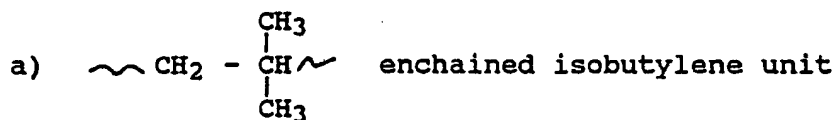
The novel versatile, pendant functionalized, backbone saturated, soluble copolymers of this invention which are derived via "clean" nucleophilic substitution reactions on a "base" terpolymer comprising isobutylene/paramethyl styrene/ and para-bromomethylstyrene are widely useful as will be further discussed in the examples dealing with specific pendant functionalities. They encompass a broad range in properties ranging from low Tg elastomers high in isobutylene to high Tg plastics high in paramethyl styrene with tough high impact compositions at intermediate isobutylene contents. The presence of appropriate pendant functionality renders this entire range of products "paintable" for use in external automotive or appliance applications, etc. and enables them to be adhered to and used as coatings on other substrates especially in exterior applications where the excellent environmental resistance of the backbone saturated copolymers is advantageous. The presence of appropriate pendant functionality also enables these compositions to react with or be coreacted with other functional polymers, or fillers, or fibers to form composite structures (i.e. laminates, dispersions, etc.) with desirable combinations of properties.

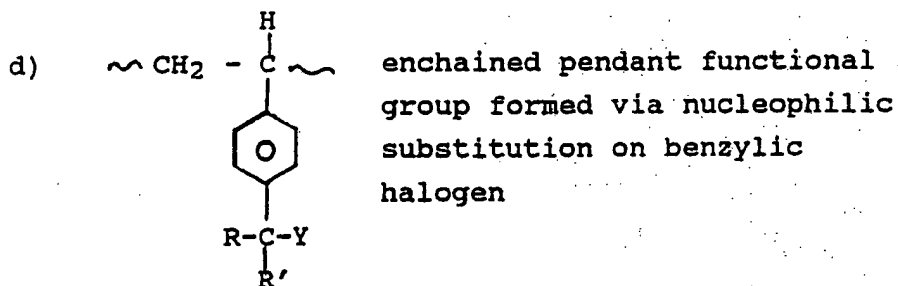
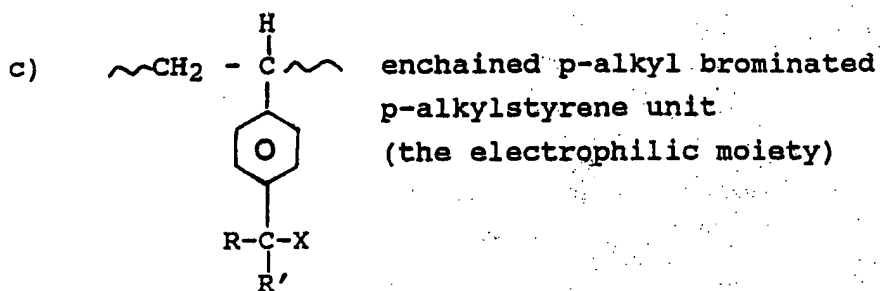
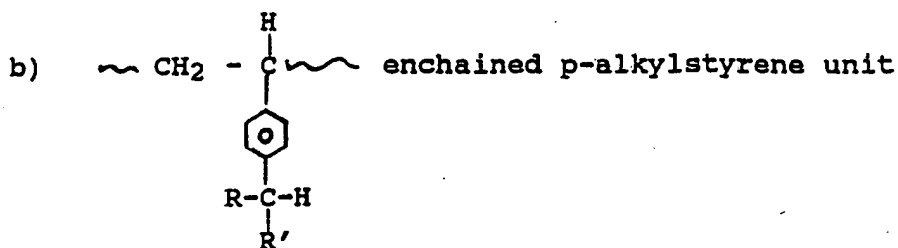
In accordance with this invention it has been found that the novel pendant functionalized saturated copolymers described and exemplified herein can be conveniently and practically produced by first preparing a base terpolymer comprising a saturated hydrocarbon backbone with one or more pendant attached electrophilic moieties, and then

- 54 -

attaching the desired new functionality via a "clean" nucleophilic substitution reaction with the pendant attached electrophilic moieties. It has been found to be desirable and is important in obtaining the pendant functionalized copolymer of this invention that the pendant attached electrophilic moieties which are replaced by other functionalities via "clean" nucleophilic substitution reactions be benzylic halogen moieties. These pendant attached electrophilic benzylic halogen moieties can be readily inserted into random isobutylene/para-methylstyrene copolymers by radical halogenation as taught in U. S. Serial No. 199,665, to yield the base terpolymer containing isobutylene/para-methylstyrene and para-methyl brominated para-methylstyrene securing random units. This base terpolymer containing electrophilic benzylic halogen moieties is the "parent" polymer from which the novel, pendant functionalized, saturated copolymers of this invention are prepared via "clean" nucleophilic substitution reactions.

These novel pendant functionalized polymers of this invention are comprised of the following "mer" units as shown on page 14:





wherein: R and R' are independently selected from the group consisting of hydrogen, alkyl, and 1° or 2° alkyl halide. X is a halogen atom (preferably bromine or chlorine, and most preferably bromine) and Y represents a new functional group attached to the polymer via nucleophilic substitution of one of the benzylic halogens so that an enchain ed c) "mer" unit has become a d) "mer" unit. Actually there can be several different Y species in the same polymer in cases where mixed functionalities are being

- 56 -

introduced. Y is the residue which becomes attached to the polymer enchain c) "mer" unit in place of halogen when a nucleophilic reagent capable of donating electrons to benzyl halides is reacted with the base terpolymer in accordance with this invention.

The four (or more if several different Y functionalities are present) "mer" units are attached to one another in random fashion to form the novel, pendant functionalized, backbone saturated polymers of this invention. Total polymer number average molecular weight can range from < 500 to > 100,000. The amounts of the various "mer" can range as follows:

- a) (isobutylene) "mer" units from 10→ 99.5 wt.%
- b) (p-alkylstyrene) "mer" units from 0.2→ 90 wt.%
- c) (radically brominated p-alkylstyrene) "mer" units from 0 → 55 wt.%
- d) (pendant functional) "mer" units from 0.1 → 55 wt.%.

Actually, there can be several different Y species in the same polymer in cases where mixed functionalities are being introduced. Y is the residue which becomes attached to the polymer unit in place of halogen when a nucleophilic reagent capable of donating electrons to benzyl halides is reacted with the base terpolymer in accordance with this invention, wherein a is about 10 to about 99.5 wt.%, more preferably about 80 to about 99, and most

- 57 -

preferably about 90 to about 98, b is about 0.2 to about 90.0 wt.%, more preferably about 1 to about 20, and most preferably about 2 to about 15, d is about 0.1 to about 55.0 wt.%, more preferably about 0.2 to about 20 and most preferably about 0.5 to about 15, and c is about 0 to about 55.0 wt.%, more preferably about 0.2 to about 20, and most preferably about 0.5 to about 15. The number average molecular weight of the functionalized polymers is from about 500 to about 1,000,000, more preferably about 30,000 to about 800,000 and most preferably about 100,000 to about 600,000.

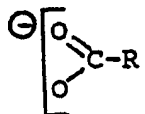
In accordance with a preferred embodiment of the present invention, the nucleophilic reagents which are capable of donating electrons to benzyl halides and to displace a halide ion via a substitution nucleophilic displacement reaction and attach the new functional group Y in the benzylic position from which the halogen was displaced may be Y or YM wherein: M is hydrogen, a metal ion, or an onium ion and Y is either a simple nucleophile containing oxygen, sulfur, silicon, carbon, nitrogen, phosphorus, or various metals; or Y is a small molecule of < 1000 molecular weight which may contain other functionality in addition to the simple nucleophile which becomes attached at the benzylic position in the nucleophilic displacement reaction.

Examples of simple nucleophiles containing oxygen which results in the attached of -O- to the benzylic position from which the halide ion was displaced included but are not limited to:

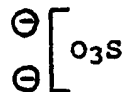
- 58 -



as in alkoxide or phenoxide



as in carboxylates



as in sodium salts

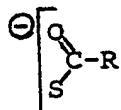
Examples of simple nucleophiles containing sulfur which result in attachment of -S- to the benzylic position from which the halide ion was displaced include (but are not limited to):



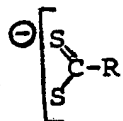
as in thiolates and thiophenolates



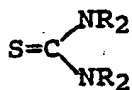
as in thioethers



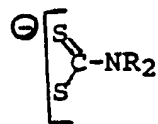
as in thiocarboxylates



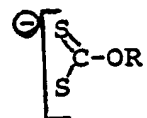
as in dithiocarboxylates



as in thioureas



as in dithiocarbamates



as in xanthates

- 59 -

\ominus SCN as in thiocyanates

Examples of simple nucleophiles containing silicon which result in the attachment of -Si- to the benzylic position from which the halide ion was displaced include (but are not limited to):

H SiR₃ as in silanes

H SiX_nR_{3-n} as in halosilanes

Examples of simple nucleophiles containing carbon which result in the attachment of -C- to the benzylic position from which the halide ion was displaced included (but are not limited to):

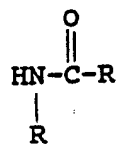
\ominus CN as in cyanides

\ominus CR₃ as in organo lithium (or other alkali or alkaline earth metals) compounds

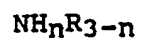
HC-(R)-(CO₂R)₂ as in malonates and di or trisubstituted methane derivatives in general in which the substituents activate the substituents methane carbon for carbon-alkylation reactions under basic conditions

Examples of simple nucleophiles containing nitrogen which result in the attachment of -N- to the benzylic position from which the halide ion was displaced include (but are not limited to):

- 60 -



as in amides

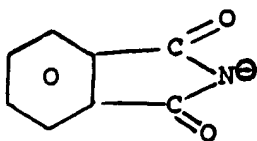


as in various amines

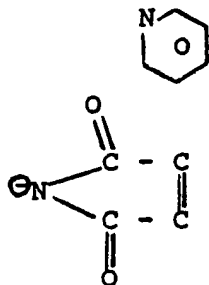


as in carbozoles

- 61 -

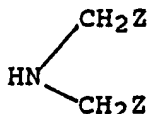


as in phthalimides

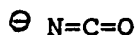


as in pyridine

as in maleimide

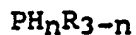


where Z is some functional group as in iminodiethanol, iminodiacetonitrile, diacetonitrile iminodiacetic acid, etc.



as in cyanates

Examples of simple nucleophiles containing phosphorus which result in attachment of -P- to the benzylic position from which the halide ion was displaced (include but are not limited to):



as in various phosphines

Examples of simple nucleophiles containing a metal which results in the attachment of -M- to the benzylic position from which the halide ion was displaced include (but are not limited to):

- 62 -

Mg- (anthracene complex in THF)

Li- (appropriately complexed)

Examples in which Y is a small molecule of < 1000 molecular weight containing other functionality in addition to the simple nucleophile which becomes attached at the benzylic position from which the halide ion was displaced in the nucleophilic displaced reaction include (but are not limited to): triethanol amine, iminodiacetic acid, iminodiacetonitrile, iminodiethanol, vinyl pyridines, cinnamate, eleostearate, linoleate, acrylate, benzoyl benzoate, benzyol phenolate, dihydroxybenzophenone, crown ethers derivatives, cryptand derivatives, cellulose derivatives, sugar derivatives, low molecular weight polyethylene oxide or polypropylene oxide chains with terminal nucleophilic groups, etc. It should be noted that these reactions in which Y contains other functionalities in addition to the simple nucleophile which becomes attached at the benzylic position from which the halide ion was displaced greatly extend the type and range of functionalities which can be incorporated into the novel pendant functionalized, saturated copolymers of this invention, as prepared by "clean" nucleophilic substitution reactions. This ability to attach multifunctional Y groups enables clusters of polar groups to be attached as is desirable in dispersants of various type (i.e. lube oil dispersants); enables functionalities that are not readily achieved by the nucleophilic displacement reaction (such as olefins or conjugated unsaturation) to be attached; and enables very complex and special

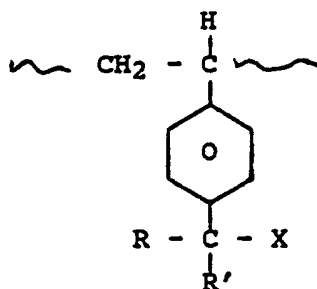
- 63 -

functionalities such as chiral compounds or crown compounds of cryptands to be attached to produce novel pendant functionalized copolymers of this invention with unique properties for highly specialized applications such as catalysts and so forth. It should also be noted that attachment of Y groups containing other functionalities requires even greater care during the nucleophilic displacement reaction by means of which the Y group are attached to insure that the new functionalities are preserved and are not consumed by sequential reactions to produce cross-linking or gelation. In some instances, it is even desirable to "block" the functionalities that need to be preserved until the nucleophilic substitution reaction is completed.

The novel and versatile, pendant functionalized, backbone saturated, soluble copolymers of this invention are prepared via "clean" nucleophilic substitution reactions on a base terpolymer comprising isobutylene/paramethyl styrene/ and para-bromomethylstyrene "mer" units enchainned in random fashion. The enchainned para-bromomethylstyrene "mer" units are the electrophiles which are the "sites" at which the "clean" nucleophilic substitution reactions are performed to attach the desired Y groups and introduce the new pendant functionality.

The enchainned electrophile, which is the site for the nucleophilic substitution reaction, has the formula:

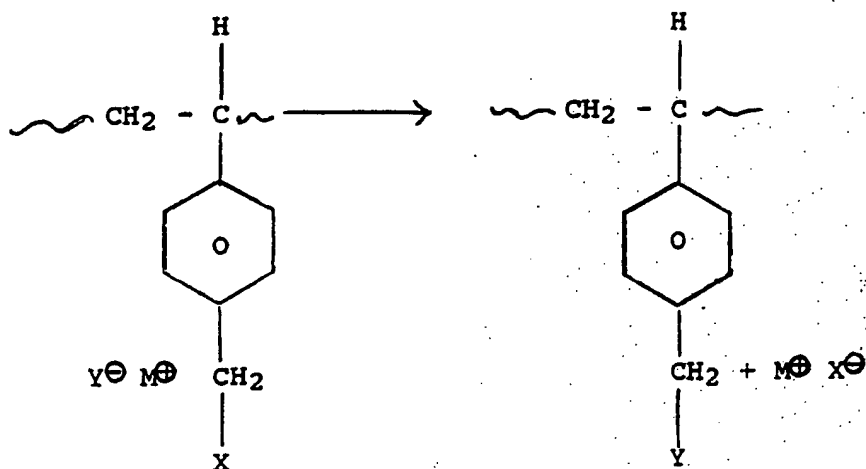
- 64 -



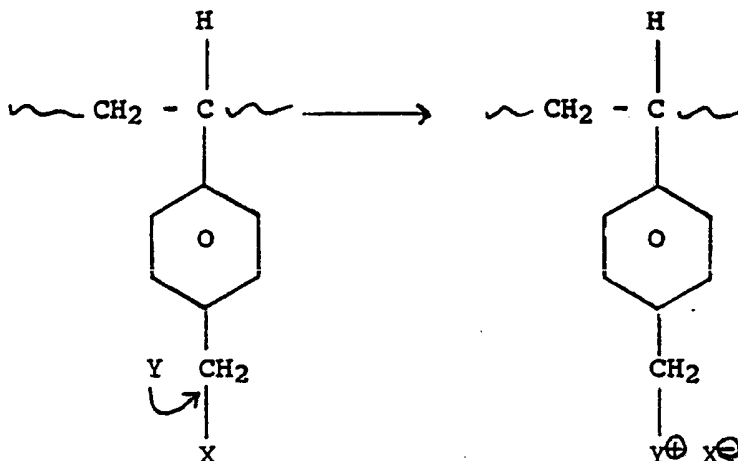
Wherein: X is a halogen (preferably bromine or chlorine) and R and R' are independently selected from the group consisting of hydrogen, alkyl preferably C₁ to C₅ alkyl, and primary and secondary alkyl halides preferably C₁ to C₅ alkyl halides.

The nucleophilic reagents which are capable of donating electrons to benzyl halides and to participate in the "clean" nucleophilic substitution displacement reaction by means of which the halide ion is displaced and replaced by the new functional group Y may be either Y or YM. Wherein: M is hydrogen, a metal ion or an onium ion and Y is either a simple nucleophile containing oxygen, sulfur, nitrogen, phosphorus, carbon, silicon, or various metals; or Y is a small molecule of < 1000 molecular weight which may contain other functionality (which is unreactive or blocked under the conditions of the nucleophilic displacement reaction). in addition to the simple nucleophile which becomes attached at the benzylic position vacated by halogen in the nucleophilic displacement reaction.

The nucleophilic substitution reactions may be set forth as follows:



or:



Nucleophilic substitution reactions of this type require the achieving and intimate contact between the reactants under the proper reaction conditions which, as already discussed, presents some problems when one of the reactants, the electrophile, is "enchained" in a high polymer chain thus making contacting more difficult and imposing restrictions on the reaction medium and conditions which may be utilized.

Most nucleophilic substitution reactions of this type also involve some degree of side reactions which can be extremely detrimental in making the pendant functionalized soluble copolymers of this invention, since even minor amounts of side reactions in high polymers can lead to gelation

- 67 -

which can greatly diminish utility. One advantage of using the unique base polymers of this invention for the nucleophilic substitutions reactions is that the undesired side reactions can be largely eliminated. It is known that nucleophilic substitution reactions can proceed by several different mechanisms and with most electrophiles these different mechanisms can lead to different products or to different amounts of side reactions. Those reactions, which proceed by a concerted S_N2 mechanism usually yield more of the desired substitution product than those proceeding by an S_N1 mechanism. An advantage of using the enchaind benzylic halogen of this invention as the electrophile site for nucleophilic substitution is that elimination reactions are entirely prevented so that even nucleophilic substitution reactions proceeding by an S_N1 mechanism still lead cleanly to the desired substitution product without undesired side reactions. A further advantage of using the preferred benzylic bromine of this invention as the site for nucleophilic substitution is that the substitution reactions proceed under mild conditions (since the benzylic bromine is so liable) so that degradation of the polymer backbone or thermal rearrangement or decomposition of the reactants or products can be avoided. Utilization of benzylic halogen, especially benzylic bromine, as the enchaind electrophile site for nucleophilic substitution as in this invention also makes it possible to select reagents and conditions so that other side reactions, such as those proceeding by another mechanism or the sequential reactions can be largely eliminated so that the soluble pendant functionalized copolymers of this

invention can be prepared by "clean" Sn nucleophilic substitution reactions. Careful observance of the six "key" requirements already outlined is necessary in order to prepare the useful, novel, and versatile, pendant functionalized backbone saturated, soluble polymers of this invention.

The exact and specific conditions suitable for preparing the various pendant functionalized, soluble, saturated copolymers of this invention will vary depending upon the new functionality being introduced as well as the base polymer composition and other factors and some experimentation may be necessary to define practical conditions in each case but the same "key" factors as outlined herein must always be considered and observed. This will become clearer in the specific examples to follow, but some general reaction conditions can first be defined. The nucleophilic substitution reactions can be run in solution using a solvent system in which both the base polymer and nucleophilic reagent are soluble; can be run in a two phase liquid run system with the base polymer dissolved in one phase and the nucleophilic reagent in the other; can be run in a two phase solid/liquid system (i.e. with the base polymer dispersed in a liquid phase containing the nucleophilic reagent) or can be run in the bulk with reactants dissolved or dispersed in the base polymer. The common solution situation is most controllable and generally the preferred case, but the bulk reaction may be economically advantageous in some cases where suitable reagents and reaction conditions can be found. The intermediate two phase systems may be advantageous under some

- 69 -

circumstances and may be necessary in instances where the solubility parameters of the base polymer (containing the electrophile) and the nucleophilic reagent are so different that no common solvents exist. In these two phase cases, it is often or usually desirable to use phase transfer catalysts to promote the nucleophilic substitution reaction at the interface between the phases or to transport the nucleophilic reagent to the electrophile site in the base polymer. A most preferred way of preparing the pendant functionalized polymers of this invention is to radically halogenate a random isobutylene/para-methylstyrene copolymer as taught in U. S. Serial No. 199,665 filed May 27, 1988, herein incorporated by reference to introduce the benzylic halogen electrophile and then conduct the nucleophilic substitution reaction to introduce the desired new functionality in the same medium in a sequential reaction (halogenate and then nucleophilically displace the halogen) without ever recovering the base halogenated polymer separately.

Depending upon the reactivity of the nucleophilic reagent used and the reaction conditions, the nucleophilic substitution reactions can be run at temperatures varying from about 0°C to about 200°C as limited by thermal stability of the nucleophilic reagent, the base polymer and the functionalized product polymer. Normally, temperatures between about 0 and about 150°C are preferred. Reaction times are normally (but not necessarily) chosen to allow the nucleophilic displacement reaction to go to completion (i.e. exhaustion of either the electrophile or the nucleophilic reagent) and

- 70 -

may range between several seconds and a few days. Normally, reaction times between a few minutes and several hours are preferred and reaction temperature and other conditions are set to make a convenient reaction time possible.

A wide range of solvents and/or solvent blends may be used as the medium in which the nucleophilic displacement reaction is run and it is this factor which determines whether a solution, dispersion, or bulk reaction is conducted. A number of factors are important in selection of the solvents. They need to be inert under the reaction conditions, easily removed from the product, easily recycled for reuse in the process, of low toxicity under use conditions with minimum environmental health concerns, and economical to use. In addition, the solvents need to provide a reaction environment which is favorable for the reaction being run that is, they must bring the reactants into the required intimate solution contact and should provide solvation stabilization for intermediate states along the desired reaction route. It is frequently necessary or desirable to use a blend of solvents to best achieve the various compromises required, with one solvent being an easily handled "good" solvent for the base polymer and the other being a "good" solvent for the nucleophilic reagent and/or providing solvation stabilization for the reaction intermediates. It is most preferred that the chosen solvent system be one that is suitable for both the radical halogenation reaction to introduce the benzylic halogen electrophile into the random isobutylene/paramethyl-

styrene copolymer, as well as for the nucleophilic substitution reaction to introduce the new pendant functionally, so that a sequential reaction route is feasible without having to recover the halogenated "base" polymer separately.

Solvents which are particularly suited for this sequential reaction route vary somewhat depending upon composition of the "base" polymer, but with the elastomeric "base" polymers high in isobutylene are the low boiling saturated hydrocarbons (C₄→C₇) or halogenated hydrocarbons (C₁→C₇). Often it is desirable to add a more polar cosolvent, such as a low boiling alcohol (C₁ - C₄) during the (second) nucleophilic displacement reaction in order to dissolve and "carry-in" the nucleophilic reagent as well as provide solvation stabilization for the nucleophilic displacement reaction. Aromatic solvents such as benzene, toluene, and chlorobenzene are generally good solvents for the base polymer over the entire composition range and provide a reaction medium favorable for many nucleophilic displacement reactions but often present other problems (i.e the toxicity of benzene or the high reactivity of toluene during radical halogenation which makes it unsuitable as the reaction medium during this first stage of the sequential reaction route). Preferred solvent composition changes as composition of the base polymer is changed and depends upon whether it is desired to run the reactions in solution or dispersion. In general solvents of higher solubility parameter containing some aromaticity or halogen are required for solution reactions with the tougher, higher T_g base

- 72 -

polymers of this invention which contain higher paramethylstyrene contents.

Similar considerations apply when considering the nucleophilic displacement reaction separately. In order to run this reaction in solution, a good solvent for the base polymer (depending upon its composition) is required and a cosolvent for the nucleophilic reagent may also be desirable or required. Good solvents for the base polymer are similar to those cited above as being suitable for the sequential reaction route, but a broader range of solvents can be considered since inertness during radical halogenation is not required. The low boiling saturated hydrocarbons ($C_4 \rightarrow C_7$) or halogenated hydrocarbons ($C_1 \rightarrow C_7$) and aromatic hydrocarbons or naphthenes are preferred. Where greater solvent polarity is desired tetrahydrofuran can be employed or good solvating agents such as dimethyl formamide or dimethyl sulfide can be added. The latter solvents are also good solvents for many of the nucleophilic reagents and may be employed along with alcohols or ketones to dissolve the nucleophilic reagent for addition to the base polymer solution. This technique of adding a solution of the nucleophilic reagent (in a solvent miscible with that used for the base polymer) with rapid stirring to the base polymer solution often results in a fine dispersion of the nucleophilic reagent so that even in cases where the nucleophilic reagent is not completely soluble in the mixed solvent resulting after the addition, an essential solution nucleophilic displacement reaction can still be run because the nucleophilic reagent

- 73 -

dissolves during reaction to replenish the solution concentration as the reaction progresses.

In more extreme cases, where the nucleophilic reagent isn't soluble in co-solvents miscible with the base polymer solvent or where the solubility of the nucleophilic reagent in mixed solvency which will retain the base polymer in solution is too low, then a two phase reaction may be run with the base polymer dissolved in one phase and the nucleophilic reagent in the other. In such cases, good mixing is essential to provide lots of interfacial contact between the reactants and a phase transfer catalyst is generally desirable to aid in transporting the nucleophilic reagent to the benzylic halogen electrophile site on the base polymer. An example might be highly polar water soluble nucleophilic reagents such as potassium cyanide, sodium sulfite, or nitrilotriacetic acid. Examples of phase transfer catalysts useful in these two phase reactors include (but are not limited to): tetrabutyl ammonium bromide, tetrabutyl ammonium bisulfate, tetrabutyl ammonium hydroxide, benzyl triethyl omonium chloride, tetrabutyl phosphonium bromide, crown ethers, cyptonds, Adogen 464, etc. These same types of materials are sometimes beneficial in speeding up the one-phase solution reaction by providing specific solvation at the reaction site.

The ultimate in working with high solids and eliminating the costs of solvent handling and recycle is, of course, to run a "bulk" reaction with the nucleophilic reagent dissolved or dispersed in

- 74 -

the base polymer. However, the bulk reaction requires use of an expensive inefficient reactor such as an extruder which is capable of providing mixing in highly viscous systems and restricts the reaction medium so that only selected nucleophilic displacement reactions are possible, and even those are more prone to involve side reactions because of the more restrictive conditions and poorer mixing which prevails during reaction.

In addition to the general reaction considerations already discussed, the factors known to influence nucleophilic substitution reactions (by those skilled in the art) may be applied in making the pendant functionalized polymers of this invention without materially affecting the invention. Thus reaction routes and activation energy can be controlled by specific solvation, or catalysts, undesired reactions can be prevented by blocking, etc.

This invention can be more fully understood with reference to the following specific examples providing details on the introduction of various pendant functionalities by nucleophilic substitution reactions on the "base" isobutylene/para-methylstyrene/para-bromomethylstyrene "base" terpolymer; wherein, unless indicated otherwise, all percentages indicated are weight percentages.

EXAMPLE 1

- 75 -

Preparation of Pendant Functionalized Iso-
butylene/Para-methylstyrene Copolymer Containing
Ionomeric S-Isothiuronium Salt Groups

IA

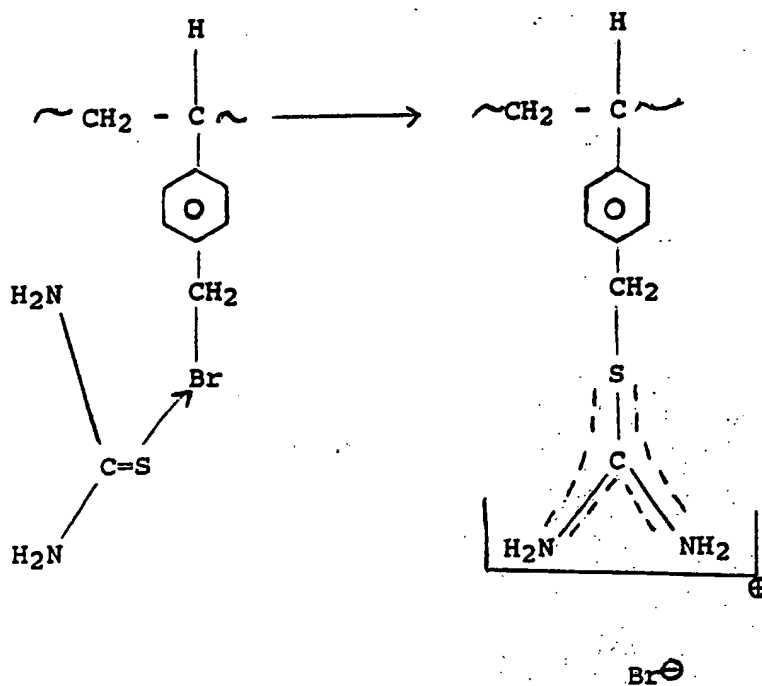
In this example, a tough ionomerically cross-linked S-Isothiuronium salt derivative of a random isobutylene/para-methylstyrene/para-bromomethylstyrene "base" polymer was prepared. The "base" polymer was prepared in accordance with the teachings of U. S. Serial No. 199,665. A random isobutylene/paramethyl styrene copolymer containing 6.6 wt.% paramethyl styrene with a viscosity oversize molecular weight of 68,000 was polymerized in the pilot plant and then radically brominated using light initiation in heptane solution in the laboratory to give a "base" polymer with a viscosity average molecular weight of 68,000 and containing 96.7 mole% isobutylene, 1.5 mole % para-methylstyrene, and 1.8 mole % paramethyl brominated paramethyl styrene. In this example (experiment) 52.7 g. of this base polymer was dissolved in 750 g. of toluene in a 1.5l resin flask under slight nitrogen purge connected through a reflux condensed to a bubbler. 2.5g of thiourea dissolved in 250 g. isopropyl alcohol was added with stirring to give a 5% solution of "base" polymer in a 75/25 toluene/alcohol solvent with 4.7 wt.% thiourea on polymer. (~ 2 moles thiourea/mole benzylic bromine). The solution was heated with stirring under nitrogen to $\sim 77^{\circ}\text{C}$ and stirred hot for 7 hours and then cooled. The polymer solution was allowed to settle and then decanted from the settled white solids (unreacted excess thiourea)). Attempts to

- 76 -

water wash the decanted polymer solutions to remove more of the unreacted thiourea were unsuccessful because it formed stable emulsions, so the polymer was recovered by precipitating and kneading in alcohol to remove unreacted thiourea. Even this proved to be difficult because the polymer solution dispersed in the alcohol and it had to be evaporated and then treated with fresh alcohol to finally recover the polymer as a mass. The recovered polymer was vacuum oven dried @ 70°C with 0.2% BHT mixed in as an antioxidant to give a spongy light tannish extremely tough ionically cross-linked elastomer.

The dried polymer was insoluble in toluene or hexane because of the ionic cross-links but dissolved readily in a 80/20 toluene/isopropanol solvent blend which solvated the ionic cross-links to give a fluid solution from which very tough elastomeric films could be cast or coatings could be applied to various substrates. Analysis on the recovered polymer showed no change in molecular weight or bromine content but the presence of the expected stoichiometric amounts of nitrogen and sulfur. NMR analysis confirmed the disappearance of the benzylic bromine and its conversion to the S-Isothiuronium salt.

- 77 -

AnalysesStarting Base Polymer

Mv	68K
wt.% Br	2.54
wt.% N	-
wt.% S	-

NMR

mole % Benzylic Br	1.8
mole % S-Isothiuronium salt	-
mole % para-methylstyrene	1.5

Pendant Functionalized Polymer

68K
2.53
0.88
1.01

1.8

1.5

IB

- 78 -

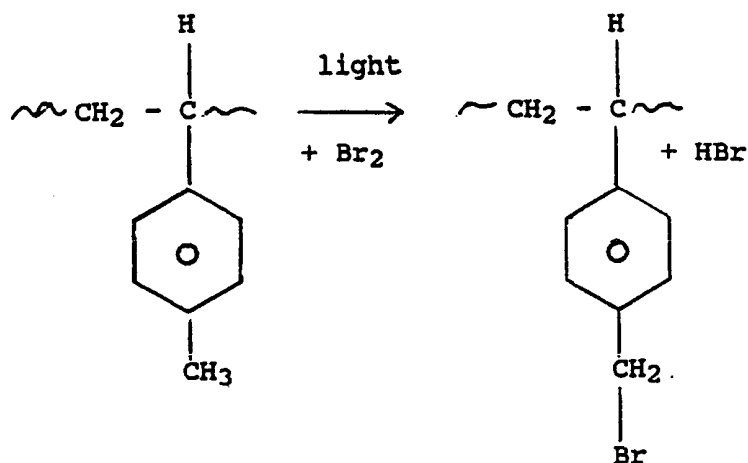
In this example, a tough ionomerically cross-linked S- Isothiouronium salt derivative of a random isobutylene/para-methylstyrene/para-bromomethylstyrene "base" polymer was prepared by a sequential reaction route with the bromination reaction followed by the nucleophilic substitution reaction without isolating or recovering the "base" brominated polymer. A random isobutylene/para-methylstyrene copolymer containing 5.8 wt.% para-methylstyrene with a viscosity average molecular weight of 350,000 was polymerized in the pilot plant one gallon continuous stirred tank reactor. 450 g. of this copolymer was dissolved in 2550 g of mole-sieve dried B&J heptane in a 5 l resin flask for radical bromination as taught in U. S. Serial No. 199,665. The flask had a glass frit immersed in the solution for nitrogen purging, had a bottom draw-off to permit washing and drawing off the aqueous layer, and was connected through a reflux condensed to a dilute caustic trap to scrub the purge gas. The 15% solution of polymer in heptane was heated to 30°C with stirring and illuminated with a 150 Watt spotlight to initiate radical bromination. Then 40.5 g of bromine (9% on polymer) diluted to 30% in dried heptane was added through a dropping funnel. After 15 minutes when the bromine color had completely faded, the light was turned off and 22 g. of 50% NaOH diluted to 350 ml. was stirred in as a quench. Then the stirrer was stopped and the basic aqueous layer was allowed to settle and was drained off. Three additional water washes were given in this way and then a sample of the cement was taken for recovery and analyses of the "base" brominated polymer.

- 79 -

To the remaining "wet" "base" polymer cement was added 40g of thiourea dissolved in 900 g. of a 50/50 heptane/isopropyl alcohol mixture and the reactor was heated to reflux at 75°C with stirring and slight nitrogen purge. It was stirred hot @ 75°C for six hours and then allowed to cool and settle. As was the case in example 1A, the functionalized polymer solution could not be water washed because it formed stable emulsions, so the polymer was recovered in isopropyl alcohol as for example 1A. It was vacuum oven dried @ 70°C with 0.2% BHT mixed in as an antioxidant. The recovered polymer was a spongy tannish extremely tough ionically cross-linked elastomer much like in example 1A but, was even more elastomeric with higher strength and better elongation. It was insoluble in heptane, or toluene because of the ionic cross-links and also unaffected by alcohol because of its composition. However, it dissolved readily in a 90/10 toluene/isopropanol mixture which disrupted the ionic cross-links by solvation.

In the first step of this sequential reaction, a portion of the enchaind paramethylstyrene moieties in the isobutylene/paramethylstyrene copolymer were converted to enchaind paramethyl moieties to produce a "base" terpolymer containing benzylic halogen (as an enchaind electrophile).

- 80 -



Analyses on the dried sample of recovered brominated polymer are shown below:

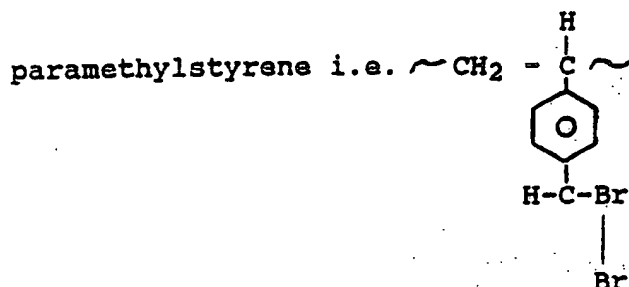
		<u>Analyses</u>	
<u>Starting Copolymer</u>		<u>Radically Brominated "Base" Terpolymer</u>	
Mv	350,000		280,000
wt.% Br	-		3.5
<u>NMR Results</u>			
Mole % PMS	2.9		0.7
Mole % Br PMS	-		1.9
Mole % Br ₂ PMS	-		0.3

- 81 -

where PMS = enchaind paramethyl styrene

Br PMS = enchaind paramethyl brominated
paramethylstyrene

and Br₂ PMS = enchaind dibrominated



In this example a very high bromine charge was used (~ 1.15 mole Br₂/mole enchaind PMS) and about 75% of the enchaind paramethyl styrene units were brominated. This high bromination level caused the observed molecular weight loss and resulted in some dibromination of the enchaind paramethyl styrene moieties. If a lower bromine charge had been used so that $<60\%$ of the enchaind paramethyl styrene units were brominated (as recommended in U. S. Serial No. 199,665), then essentially no dibromination would have occurred and there would have been essentially no molecular weight loss.

In the second step of this sequential reaction; a portion of the enchaind para-bromo-methylstyrene units were converted to S- isothiuronium salt units as in example 1A. In this, example the nucleophilic substitution reaction as run at 75°C for 6 hours in an 87/13 heptane/alcohol solvent at a 10 wt.% base polymer concentration with

- 82 -

3 mole of thiourea/mole of benzylic bromine.
Analyses on the recovered polymer are shown below:

	<u>"Base" Terpolymer</u>	<u>Pendant Functionalized Polymer</u>
Mv	280,000	280,000
wt.% Br	3.15	3.0
wt.% N	-	0.45
wt.% S	-	0.5
Mole % Br PMS	2.2	1.3
Mole % S- Isothiouronium salt	-	0.9
Mole % PMS	0.7	0.7

In this reaction only a portion of the benzylic bromines were replaced by S-isothiouronium salt groups despite the larger molar excess of thiourea used because the wet 87/13 heptane/alcohol blend used this experiment is a less favorable reaction medium in which to run the nucleophilic displacement reaction than the 75/25 toluene/isopropanol mixture used in example 1A. The rate of nucleophilic displacement reactions are strongly influenced by the reaction medium and solvation, and these factors can be used to control reaction rate.

In this nucleophilic substitution reaction about half of the benzylic bromine was converted to S-isothiouronium salt to give a functionalized polymer containing both benzylic bromine and S-isothiouronium salt functionality. This mixed functionality polymer is very interesting because not only is it a tough elastic material due to the ionic cross-links but it also contains active benzylic

- 83 -

bromine functionality which can be utilized for other reactions including forming covalent permanent cross-links in many ways. In fact this mixed functionality polymer containing both benzylic bromine and S-isothiuronium salt functionalities forms permanent covalent cross-links simply by heating above 100°C probably via an, N-alkylation reaction between an attached thiourea group and an unconverted benzylic bromine on another chain with formation of a cross-link and release of HBr - it is preferred to have an acid scavenger such as zinc oxide present to pick up the released HBr and stabilize the cross-linked polymer in situations where this permanent cross-linking is desired.

To demonstrate the reversible ionic cross-links and permanent covalent cross-links upon heating: A portion of the mixed pendant functionalized polymer of this example was dissolved in a 90/10 toluene/isopropanol solvent blend as a 15% solution and cast on a glass plate as a film by allowing the solvent to evaporate and deposit a tough rubber film. Drying was completed in a vacuum oven at 70°C. A very tough elastomeric film was deposited on the glass with very strong adhesion. The film could not be removed by toluene, heptane, or alcohol. However, a portion of the film was exposed to a 90/10 toluene/isopropanol mixture and redissolved. Another portion of the film was placed in a vacuum oven @ 120°C for 2 hours - it had darkened somewhat, but was still a very tough, strongly adhered elastomeric film. During the heating though it had formed covalent cross-links as shown by the fact that it could no longer be

- 84 -

dissolved and removed even in a toluene/isopropanol solvent blend. The blend only served to swell the film - but did not dissolve it or remove it from the glass.

The S-isothiuronium salt pendant functionality impacts very interesting and useful properties to the "base" polymer. The salt is a strong cationic ionomer and the salt groups associate in the polymer/(hydrocarbon) matrix to provide strong ionic cross-links. It is also a strongly hydrogen bonding group because of the NH hydrogens and the reversible cross-links involve hydrogen bonding. This hydrogen bonding ability also permits associations with other groups and enhances adhesion to many surfaces. Another desirable characteristic for some uses is that the ionic groups do not contain any metal ions. And the ability of the mixed functionality polymer of this example to form permanent co-valent cross-links by heating adds yet another characteristic useful in some applications. Clearly this pendant cationic S-isothiuronium salt pendant functionality is very interesting and useful in selected applications. it is a strong cationic ionomer with strong hydrogen-bonding propensity.

1C

In this example, a tough ionomerically cross-linked S-isothiuronium salt derivative of a random isobutylene/paramethylstyrene/para-bromomethylstyrene "base" polymer was prepared and converted to salts with various anions. The "base" polymer was prepared in accordance with the

- 85 -

teachings of U. S. Serial No. 199,665. A random isobutylene/paramethylstyrene copolymer containing 7.0 mole % paramethyl styrene with a Mooney viscosity of 30.2 ($M_L(H8)$ @ 125°C) was polymerized in a blocked operation in an 1800 gallon continuous reactor using commercial butyl plant facilities and then radically brominated using VAZO 52 initiation in heptane solution in a 100 gallon glass lined pfaudler reactor to give a "base" polymer with a Mooney viscosity of 29 and containing 2.0 mole% paramethylstyrene, 5.0 mole% paramethylstyrene, and 93 mole % isobutylene. In the nucleophilic substitution reaction, 450 g. of the "base" polymer was dissolved in 2750 g of toluene in a 5 l resin flask under slight nitrogen purge connected through a reflux condenser to a bubbler. 38.5 g of thiourea (3 moles/mole benzylic bromine) dissolved in 907 g isopropanol was added with stirring to give an 11% "base" polymer solution in a 75/25 toluene/isopropanol solvent blend. The solution was then heated with stirring under sl.N₂ purge to reflux @ 86°C. The thiourea partially precipitated and was initially partially present as fine dispersed crystal in the mixed solvent at room temperature but gradually dissolved or the solution was heated and the nucleophilic substitutions reaction progressed. The solution was stirred hot at 86°C for 6 hours and then cooled and allowed to settle so that the pendant functionalized polymer solution could be disconnected from the settled unreacted excess thiourea. As in the other examples the solution of the S-isothiuronium salt functionalized polymer could not be water washed because it formed stable emulsions, but a portion was shaken with an equal

- 86 -

volume of water to yield a stable emulsion anyway and the emulsion was set aside for other work. Meanwhile a portion of the polymer was recovered by precipitation in isopropanol. It was kneaded to wash out unreacted thiourea and then further purified by redissolution in 90/10 toluene/IPA and then reprecipitation in isopropanol. This purified functionalized polymer was vacuum oven dried @ 70°C with 0.2 wt.% BHT mixed in as an antioxidant. This dried recovered polymer was a spongy light tan extremely tough ionically cross-linked elastomer as in the previous examples. It was insoluble in hydrocarbons or alcohols but readily dissolved in a 90/10 toluene/isopropanol mixture.

Analyses showed a complete conversion of the benzylic bromines to S-isothiuronium bromide salt as shown below:

Analyses

<u>"Base" Terpolymer</u>		<u>S-Isothiuronium Bromide Pendant functionalized Polymer</u>
Mv	280K	280K
wt.% Br	3.0	2.5
wt.% N	-	0.88
wt.% S	-	1.0
<u>NMR</u>		
Mole % Benzylic Br	2.0	-
Mole % S-Iso-thiuronium bromide	-	2.0
Mole % Paramethyl Styrene	5.0	5.0

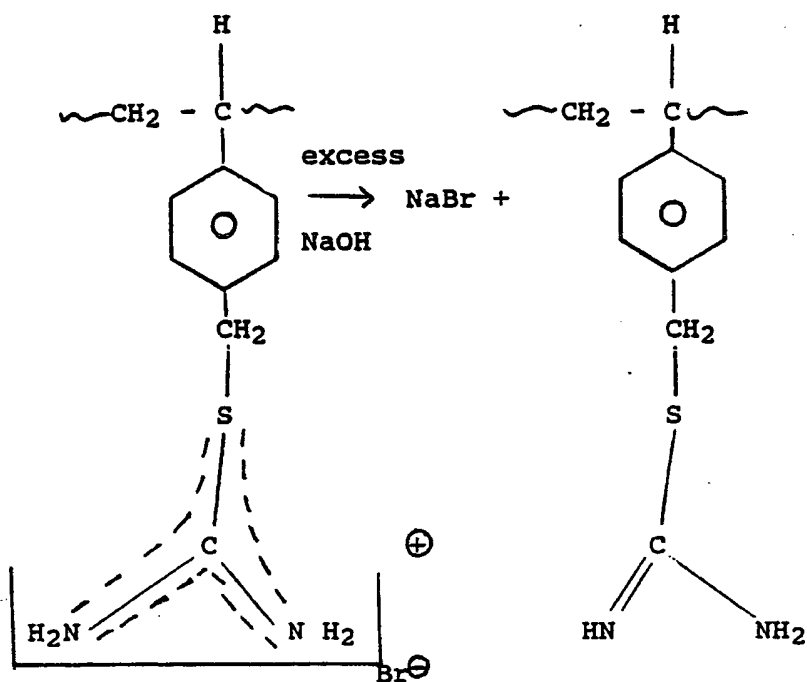
The stable emulsion formed by shaking the S-isothiuronium salt functionalized polymer in the

- 87 -

75/25 toluene/isopropanol reaction solvent with water had a pH of ~ 6 . Dilute NaOH solution was added to a portion of this emulsion to raise the pH to 10 and the basic emulsion was shaken; it separated at once to a clear basic water layer and a gelatinous swollen polymer layer. This layer could not be redispersed by shaking it with fresh water or water/alcohol mixtures - so after several attempted washes the polymer was recovered by precipitation in isopropanol. Recovery was very difficult because the gelatinous mass was so tough and the solvent extracted very slowly. The recovered polymer was permanently cross-linked and insoluble in anything. Analyses showed that most of the bromine and about half of the nitrogen was lost, but all of the sulfur was still present.

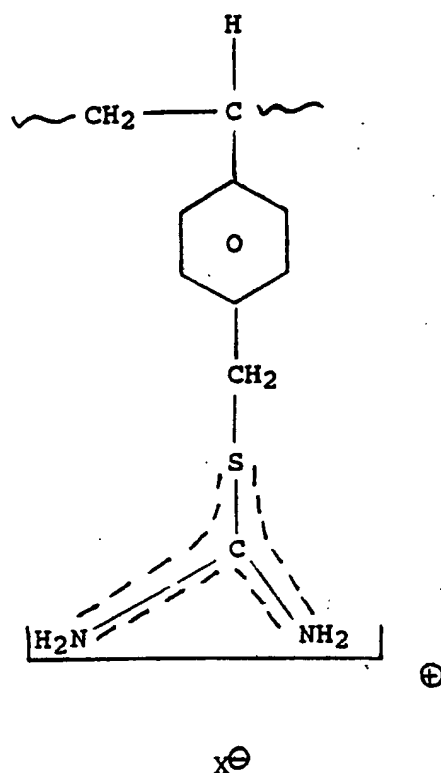
Shaking with excess base apparently destroyed the emulsion by freeing the S-alkyl thiourea from the bromide salt as shown:

- 88 -



but the S-alkyl thiourea derivative was unstable in the basic solution and rapidly decomposed (via hydrolysis, etc.) to yield a cross-linked polymer.

Other portion of the stable emulsion @ pH ~ 6 were carefully neutralized cold with dilute caustic and then acidified with various acids (HCl , H_2SO_4 , acetic etc.) and reshaken to form in each case stable emulsions from which the polymer was recovered by precipitation in isopropanol (sometimes requiring a partial evaporation of solvent before the polymer would mass together to permit kneading and washing). In this way, various isothiuronium salt derivatives were recovered:



wherein X was Cl^- , HSO_4^- , $\text{CH}_3\text{C}(\text{O})\text{O}^-$, etc.

The salts were all soluble in a 90/10 toluene/isopropanol mixture and tough ionomerically cross-linked coatings could be deposited on various substrates from these solutions by evaporating the solvent.

As is discussed in later examples with other cationic ionomer pendant functionalized derivatives of this invention, the various salts are

- 90 -

also easily converted to latexes by stripping the solvent from the stable emulsion to give stable aqueous dispersions (latexes) of the ionomerically cross-linked particles from which coatings can be deposited.

Either the solutions or latexes of these S-isothiuronium salt derivatives are also useful as adhesives, binders, etc.

Example 2

Preparation of Pendant Functionalized Isobutylene/Paramethyl Styrene Copolymer Containing Ionomeric Quaternary Ammonium Salt Groups.

2A

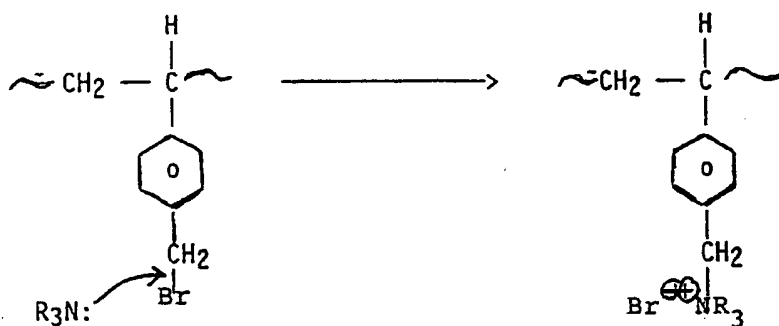
In this example, a tough ionomerically cross-linked quaternary ammonium salt derivative of a random isobutylene/para-methylstyrene/para-bromomethylstyrene "base" polymer was proposed. The "base" polymer was prepared in accordance with the teachings of U. S. Serial No. 199,665. A random isobuthylene/para-methylstyrene copolymer containing 4.8 wt.% para-methylstyrene and a Mooney viscosity of 30 ($M_L(H8)$ @ 125°C) was polymerized in a commercial 1800 gallon butyl polymerization reactor and then radically brominated using VA20 52 initiation in hexane solution in a 100 gallon glass-lined pfaudler Br reactor to give a "base" terpolymer with a Mooney viscosity of 29 with 2.6 wt.% bromine. The "base" terpolymer composition was 1.4 mole % para-

- 91 -

bromomethylstyrene (including ~ 0.1 mole% dibrominated paramethylstyrene) 0.9 mole% paramethylstyrene and 97.7 mole% isobutylene (there was a small amount of dibromination and slight molecular weight loss due to the relatively high bromination level of $\sim 61\%$ of the para-methylstyrene "mer" units. In the nucleophilic substitution reaction, 450 g of the "base" terpolymer were dissolved in 2800 g of toluene in a 5 l. resin flask under slight nitrogen purge and connected through a reflux condenser to a scrubber and bubble to give a 13.85 wt.% solution. Then 47.2 g of triethyl amine dissolved in 700 g. of isopropanol were added slowly with stirring to give on 11.4% solution of "base" terpolymer in an 80/20 toluene/isopropanol solvent blend with ~ 3 moles triethanol amine per mole of benzylic bromine. The solution was then heated with stirring to reflux at $85 \rightarrow 86^\circ\text{C}$ under slight nitrogen purge. The solution was stirred at reflux for 6 hours and then allowed to cool under nitrogen. A trial on an aliquot showed that the solution emulsified when shaken with water or water/alcohol (70/30) mixtures so it could not be washed. The emulsions had a pH of ~ 8 . It remained stable when acidified and even when the pH was raised to 10 \rightarrow 11 with NaOH solution would still not separate well. Hence the functionalized polymer was recovered by precipitation and kneading in isopropanol and further freed of unreacted triethyl amine by redissolution in a toluene/isopropanol blend and reprecipitation in isopropanol. The purified functionalized polymer was vacuum oven dried at 70°C after 0.2 wt.% BHT had been mixed in as an antioxidant. The dried recovered polymer was a spongy slightly off-white extremely tough

- 92 -

ionically cross-linked elastomer. The pendant cationic quaternary ammonium salt groups which had become attached to the "base" terpolymer by nucleophilic displacement of the benzylic bromines self-associated to give a tough ionically cross-linked elastomer. It was insoluble in hydrocarbons or alcohols but readily dissolved in a 90/10 toluene/isopropanol mixed solvent which disrupted the ionic cross-links by solvation. The nucleophilic displacement reaction is shown below:



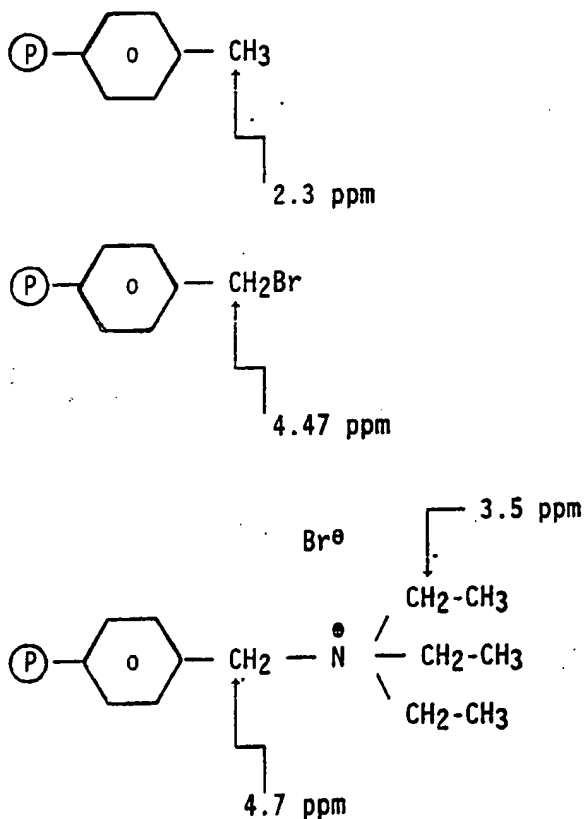
Analyses as summarized below showed essentially complete substitution of benzylic bromines had occurred to give the pendant quaternary ammonium salt functionalized polymer.

	<u>Analyses</u>	
	<u>Starting</u> <u>"Base" Terpolymer</u>	<u>Pendant</u> <u>Functionalized Polymer</u>
Mv	270,000	270,000
wt.% Br	2.6	2.2
wt.% N	\	0.34
<u>NMR</u>		
mole% Benzylic Br	1.4	\
mole% Quat.	\	1.4
mole% Paramethylstyrene	0.9	0.9

The proton NMR spectra showed the disappearance of the resonances at 4.47 ppm due to the benzylic hydrogens adjacent to the bromine and the appearance of two new resonances: one at 4.7 ppm due to the benzylic hydrogens adjacent to the quaternary nitrogen and another at 3.5 ppm due to the methylene hydrogens adjacent to the quaternary nitrogen. The resonances at 2.3 ppm due to the paramethyl hydrogens of the enchaind paramethyl styrene "mer" units remained unchanged by the nucleophilic substitution reaction:

PROTON NMR RESONANCES FOR ENCHAIND

"MER" UNITS



- 94 -

A portion of the dried pendant functionalized polymer of this example was dissolved in a 90/100 hexane/isopropanol solvent blend to give a 15 wt.% solution. This solution was cast on a glass plate and allowed to evaporate to deposit a tough rubbery film. Drying was completed in a vacuum oven at 70°C. An extremely tough ionically cross-linked film with excellent adhesion to the glass was deposited in this way. The film could be dissolved off again with the mixed hydrocarbon/alcohol solvent blend. In a similar manner a film of tough ionically cross-linked elastomer was deposited on several porous substrates (i.e. coarse woven fabrics) by impregnating the substrates with the solution by dipping and then allowing the solvent blend to evaporate to produce a "proofed" fabric coated with a tough ionically cross-linked elastomer. The "proofed" fabrics were water resistant with water droplets simply "beading-up" and running off when applied. They would also be expected to possess the high germicidal properties characteristic of quaternary ammonium salts. This quaternary ammonium salt functionalized polymer would also be useful in many adhesives and binder applications where its high strength, toughness, water resistance, germicidal properties, environmental resistance and good aging properties would be beneficial. It would also function well as a corrosion-resistant coating on metals where the water resistance, environmental resistance, good adhesion and corrosion-inhibiting properties of cationic ionomers would be desirable. The ability to self-cross-link through ionic associations without the need to add vulcanization agents (with their

- 95 -

attendant problems of extractability, toxicity, cost, etc.) or be subjected to a heated vulcanization step is a highly desirable property of this cationically functionalized polymer.

2B

In this example a pendant functionalized primarily isobutylene-based copolymer containing cationic quaternary ammonium salt groups was prepared and converted to an emulsifier-free stable latex. An isobutylene-based polymer with an M_v of 45,000 and containing 2.0 mole% para-chloromethylstyrene "mer" units was dissolved in a 70/30 toluene/isopropanol solvent blend to form a 35% solution by overnight shaking in a 2 gallon container. This solution was charged along with 1.4 times the stoichiometric amount of triethyl amine (based on the amount of benzylic Chlorine) to a 51 resin flask set-up as described in Example 2A and heated to 82°C with stirring for 4 hours to complete the nucleophilic substitution reaction. A sample of the pendant functionalized polymer was recovered for analysis as outlined in Example 2A by precipitation and kneading in isopropanol, resolution in toluene/isopropanol and reprecipitation in isopropanol before vacuum-oven drying at 70°C with 0.2 wt.% BHT mixed in as an antioxidant. The purified, dried, recovered pendant functionalized polymer was an extremely tough white crumb which was ionomerically cross-linked as shown by insolubility in toluene, but ready solubility in a 90/10 toluene/isopropanol solvent blend. Analysis showed that complete conversion of benzylic chlorines to

- 96 -

quaternary ammonium salt groups had occurred. The recovered polymer contained 0.48 wt.% nitrogen and NMR analysis showed the presence of 2.0 mole% benzyl triethyl ammonium chloride salt groups.

The balance of the cooled solution resulting from the nucleophilic substitution reaction was simply mixed "as is" with distilled water at a 40/60 water/solution ratio by volume to give a stable oil-in water emulsion which was refined first with a dispersator and then in a colloid mill to give a very stable fine particle size raw latex. The raw latex was stripped by heating with stirring under nitrogen to remove the solvents and part of the water to give a stable finished latex containing 50% solids. No emulsifiers were required in making the latex and the preparation and stripping, were accomplished easily with no foaming problems as are normally experienced in preparing, stripping and concentrating latexes containing added "soaps" as emulsifiers.

Castings from the finished latex dried to clear, hydrophobic, rubbery, tough, ionomerically cross-linked films as described for the solution cast films of Example 2A. This emulsifier-free cationic latex makes possible the use of this tough, ionically cross-linked cationically functionalized polymer in a host of applications, including dipped goods, binders, nonwovens, coatings, etc., which could benefit from its excellent aging and environmental resistance along with its other "unique" properties.

- 97 -

The ability of the pendant attached quaternary ammonium salt groups to stabilize the emulsion and latex so that no added "soaps" are required, and then to self-associate in the deposited film to provide "ionomeric" cross-links is especially important. The added "soaps" required as emulsifiers in most latexes have many drawbacks associated with them, such as: they promote foaming; they interfere with adhesion of the latex polymer to fillers or fibers used as reinforcing agents, and interfere with adhesion of the latex polymer to surfaces or substrates it is deposited on; they are extractable to create applications problems including toxicity and environmental concerns; they can migrate to the surface of the deposited films or to interfaces in filled deposited films to create problems; they impart hydrophilicity and enhance water absorption in deposited coatings, etc. In the emulsifier-free cationic latexes of this invention, all these drawbacks are eliminated. The pendant quaternary ammonium salt groups provide emulsion stabilization in the latex, but then self-associate to provide ionic cross-links in the dried polymer so that it is hydrophobic with less water absorption and with excellent adhesion to substrates it is deposited on or to fibers or fillers dispensed in it.

2C

In this example, an attempt to prepare a quaternary ammonium salt derivative of a random isobutylene/paramethylstyrene/para-bromomethylstyrene "base" terpolymer was unsuccessful because

- 98 -

reaction conditions were not properly chosen. In this example, the same "base" terpolymer used in Example 2A was used. Its composition was 1.4 mole% para-bromomethylstyrene, 0.9 mole% paramethylstyrene and 97.7 mole% isobutylene with a viscosity average molecular weight of about 270,000. In the attempted nucleophilic substitution reaction, 450 g. of this "base" terpolymer was dissolved in 3,500 g. of heptane to give an 11.4% solution and then 47.2 g. of triethyl amine was added and stirred in (0.3 m triethyl amine/mole benzylic bromine). The solution was heated to 90°C with stirring under slight nitrogen purge and kept hot for 7 hours before being allowed to cool. In this case, the polymer solution had little tendency to emulsify when shaken with water but separated quickly and cleanly as is usual for solutions of the "base" terpolymer. Recovery of the polymer as outlined in Example 2A by precipitation, resolution, and reprecipitation followed by vacuum-oven drying at 70°C gave a dried polymer which was indistinguishable from the starting "base" terpolymer. Analysis showed all the benzylic bromines remained and there was no nitrogen or quaternary ammonium salt groups present. Despite the fact that the same "base" terpolymer was used with the same stoichiometric excess of triethyl amine and an even hotter reaction temperature for a longer time than in Example 2A, no nucleophilic substitution occurred because the heptane solvent used is not a good solvating agent for intermediates along the desired reaction route. Heptane is not a favorable medium for the quaternization reaction: it does not facilitate the nucleophilic substitution reaction by solvation at the reaction site as does

- 99 -

the mixed toluene/isopropanol solvent blend used in Example 2A. This example shows the importance of observing the "key" requirements as outlined in this invention in order to produce the pendant functionalized polymers claimed.

Example 3

Preparation of Pendant Functionalized Isobutylene/Substituted Para-methylstyrene Copolymer Containing Ionomeric Quaternary Phosphonium Salt Groups

In this example, a pendant functionalized primarily isobutylene-based copolymer containing cationic quaternary phosphonium salt groups was prepared and converted to a stable, emulsifier-free latex. An isobutylene-based polymer with an M_v of 17,000 and containing 1.9 mole% para-chloromethylstyrene "mer" units was dissolved in a dried 75/25 heptane/isopropyl alcohol solvent blend under nitrogen to form a 40% polymer solution in a 5l resin flask. The reactor was connected through a dry ice-cooled cold finger (set-up to reflux condensables back into the flask) to a scrubber for vented gasses and bubbler to maintain several inches of water positive pressure on the reactor. A slow dry nitrogen flow was maintained through the system to maintain the reactants under a dry, inert atmosphere. With stirring at 25°C and while maintaining the dry nitrogen seal, twice the stoichiometric amount of triethyl phosphine (on benzylic chlorine) as a 67% solution in isopropanol was allowed to drip in slowly from a sealed dropping funnel. The mixture was heated with stirring to reflux at 77°C

- 100 -

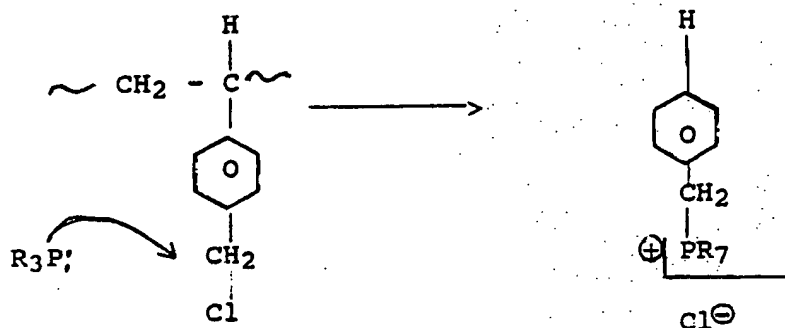
and stirred for 2 hours at reflux under nitrogen before being cooled. A sample of the pendant functionalized polymer was recovered from the resulting clear fluid solution for analysis by precipitation and kneading in isopropanol, resolution in hexane/isopropanol, and reprecipitation in isopropanol followed by vacuum-oven drying at 70°C with 0.2% BHT mixed in as an antioxidant. Despite the very low molecular weight, the recovered polymer was a tough elastomeric ionically cross-linked polymer very unlike the soft, sticky, semi-fluid starting "base" polymer. Analysis showed it contained 0.95 mole% phosphorus indicating about a 50% conversion of benzylic chlorines to quaternary phosphonium salt groups had occurred.

The remaining cooled solution from the nucleophilic substitution reaction was simply mixed "as is" with distilled water at a 40/60 water/solution ratio by volume to give a stable oil-in-water emulsion which was refined and then stripped and concentrated as in Example 2B to give a stable, emulsifier-free fine particle size cationic latex at 50% solids by weight. As in Example 2B, the latex preparation and stripping was accomplished easily with no foaming problems, and castings from the latex dried to hydrophobic, clear, tough, ionically cross-linked elastomeric films which would be useful in a broad spectrum of applications as already outlined. The pendant functionalized polymer of this latex contained mixed functionalities, benzylic chlorines and quaternary phosphonium chloride salt groups because the nucleophilic substitution reaction had not gone to

- 101 -

completion. Nevertheless, the presence of 1% quaternary phosphonium chloride salt groups was adequate to permit preparation of the stable emulsifier-free latex, and was adequate to provide ionic cross-linking in deposited polymer films. The presence of the benzylic chlorine would permit permanent covalent cross-link to be formed in many ways or permit other reactions to be run on this useful pendant functionalized polymer.

The nucleophilic substitution reaction is shown below:



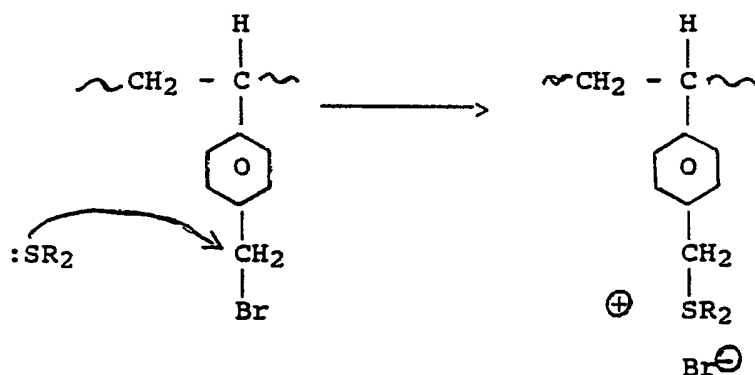
Analysis showed that the reaction was accomplished without degradation or cross-linking and under the conditions of this experiment achieved a 50% conversion of benzylic chlorines to quaternary phosphonium chloride salt groups. Higher conversions could be achieved with longer reaction times and/or higher reaction temperature -- or by choosing a more favorable reaction medium.

Examples 1-3 all show that the backbone saturated pendant functionalized copolymers of this invention containing various cationic pendant

- 102 -

functionality are readily prepared by following the procedures of this invention; and that they have useful combinations of properties for various applications. The pendant cationic groups are capable of imparting self-emulsification properties to make possible the facile preparation of emulsifier-free cationic latexes and the pendant cationic groups self-associate in dry deposited films to provide ionic cross-links which are reversible by proper solvation.

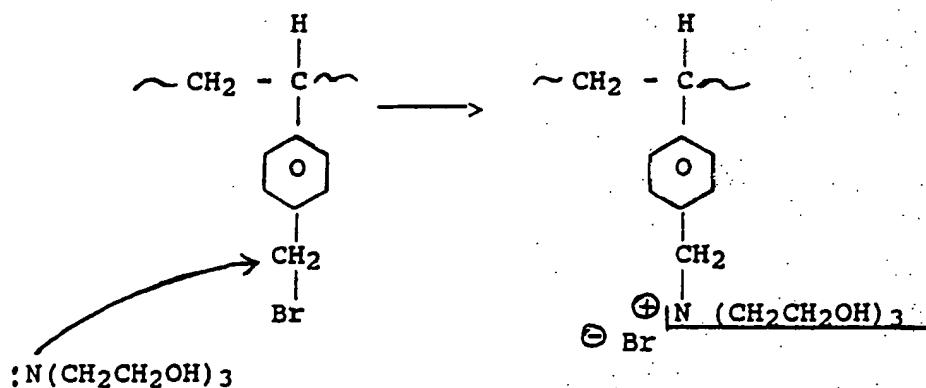
Three classes of cationic pendant functionalized copolymers have been exemplified (i.e. S-isothiuronium salts, quaternary ammonium salts, and quaternary phosphonium salts), but others such as the sulfonium salts using thioethers as the nucleophile as shown below are also possible:



Properties of these cationic pendant functionalized polymers can be varied and controlled by the type of cationic group attached as well as by the R groups present and the counterion so that a broad range of properties is possible. Thus, while we have exemplified only the triethyl quaternary ammonium and phosphonium salts, the quaternary salts with other R groups are readily prepared to impart modified

- 103 -

properties. Generally as the R groups become smaller (i.e. from ethyl to methyl), the ionic associations become stronger and more difficult to disrupt, but hydrophobicity improves as the R groups become larger. Properties are also strongly influenced by the counterion (i.e. chloride, bromide, bisulfate, etc.). Similarly properties of the S-isothiuronium salts are strongly dependent upon whether thiourea itself (as used in our examples) or substituted thioureas are used as the nucleophile. Strength of the ionic cross-links and hydrogen bonding properties are both diminished as substituted thioureas containing more and longer R groups are used to prepare the salts. Also the R groups themselves can contain other functionality to prepare cationic salts containing other useful functionality as for instead using triethanol amine as the nucleophile to prepare a pendant functionalized polymer containing quaternary ammonium salt groups with hydroxy functionality to permit further reactions or promote adhesion or dispersant action, etc.:



In addition, although not exemplified herein, it would be obvious to one skilled in the art that pendant anionic groups could also be attached to

- 104 -

prepare anionic pendant functionalized polymers such as carboxylates or sulfonates.

Example 4

Preparation of Pendant Functionalized Isobutylene/Paramethylstyrene Copolymer Containing Hydroxy Functionality

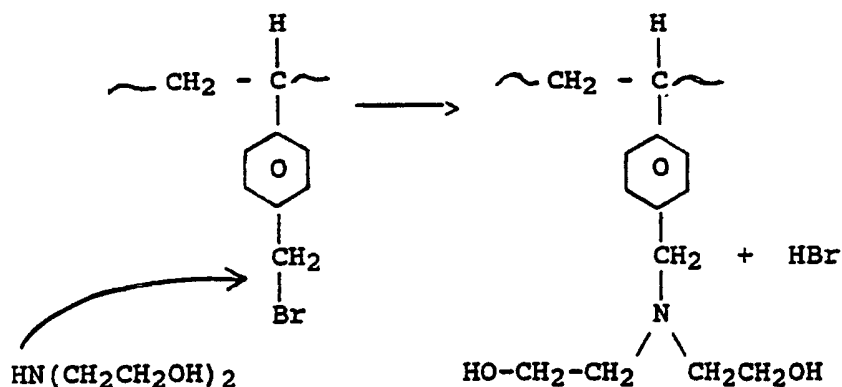
4A

In this example, pendant functionality was attached to a random isobutylene/paramethylstyrene/para-bromomethylstyrene "base" terpolymer by nucleophilic substitution using diethanol amine as the nucleophilic reagent. The "base" terpolymer was prepared in accordance with the teachings of U. S. Serial No. 199,665. A random isobutylene/paramethylstyrene copolymer containing 4.7 wt.% paramethylstyrene with a viscosity average molecular weight of 140,000 was polymerized in the pilot plant and then radically brominated using VAZO 52 initiation at 60°C as a 15% solution in hexane in a 100 gallon glass-lined pfaudler reactor to give a "base" terpolymer with a viscosity average molecular weight of 135,000 containing 1.6 wt.% bromine. The "base" terpolymer composition was 0.9+ mole% para-bromomethylstyrene, 1.4 mole% paramethylstyrene, and 97.7 mole% isobutylene. In the nucleophilic substitution reaction, 750 g. of the "base" terpolymer were dissolved in 2438 g. of toluene in a 5l resin flask set-up as in Example 2A by stirring under nitrogen to form a 23.5 wt.% solution. Then 48 g. diethanol amine (3 moles/mole bromine) in 610 g. of isopropanol was added slowly with stirring at room temperature to give a

- 105 -

19.7 wt.% polymer solution in an 80/20 toluene/isopropanol solvent blend with 3 moles/mole of bromine of the nucleophilic reagent. The solution was heated with stirring under N₂ to reflux at \wedge 87°C and stirred at reflux for 7 hours before being allowed to cool. Several samples were taken during the reaction to determine when the reaction was completed. All the samples and the final solution emulsified when shaken with water or water/isopropanol so that it was not possible to wash out the unreacted diethanol amine. As shaken, the emulsions had a pH of \wedge 8, but were stable even when made more basic or acidified so that the polymer was recovered by precipitation and kneading in isopropanol. The recovered "wet" polymer was further purified by washing and kneading in a 50/50 water/methanol mixture to complete the extraction of unreacted diethanol amine and then vacuum-oven dried at 70°C with 0.2 wt.% BHT mixed in as an antioxidant. As recovered under basic conditions (due to the presence of unreacted, diethanol amine), the pendant functionalized polymer was a slightly off-white, opaque, tough, rubbery polymer only slightly tougher than the sticky "base" terpolymer and still soluble in hexane. Analysis as summarized below showed the loss of most of the bromine with an essentially complete conversion of benzylic bromine to imino diethanol pendant functionality:

- 106 -

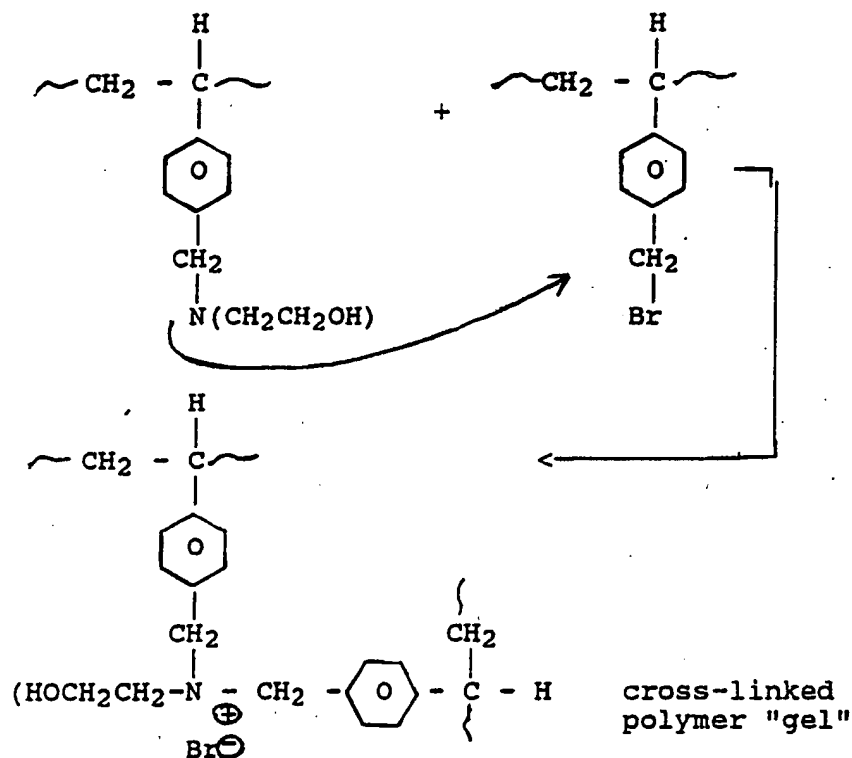
Analyses

	"Base" <u>Terpolymer</u>	Pendant <u>Functionalized Polymer</u>
M_v	135,000	~130,000
Wt% Br	1.6	0.2
Wt% N	-	0.28
<u>NMR</u>		
Mole% Benzylic Br	0.9	-
Mole% Imino diethanol	-	0.9
Mole% OH	-	1.8

Samples taken after 2 and 4 hours at reflux were identical to the final product but the sample taken just as the reaction started to reflux was cross-linked after oven drying and was insoluble in anything so that NMR analyses could not be done. Elemental analysis showed the presence of slightly more bromine (0.33 wt.%) and slightly less nitrogen (0.25 wt.%), indicating the nucleophilic substitution reaction had not yet gone to completion and the

- 107 -

cross-linking probably involved a sequential reaction of already attached iminodiethanol amine pendant functionality with unreacted benzylic bromine to form a quaternary ammonium salt cross-link during drying:



Apparently, under the conditions of this example, the nucleophilic substitution reaction had completely replaced the benzylic bromines within 2 hours at reflux temperature; and the reaction must be pushed to completion in the presence of excess diethanol amine nucleophilic reagent or sequential reactions involving already attached nucleophilic iminodiethanol pendant functionality will produce cross-linking.

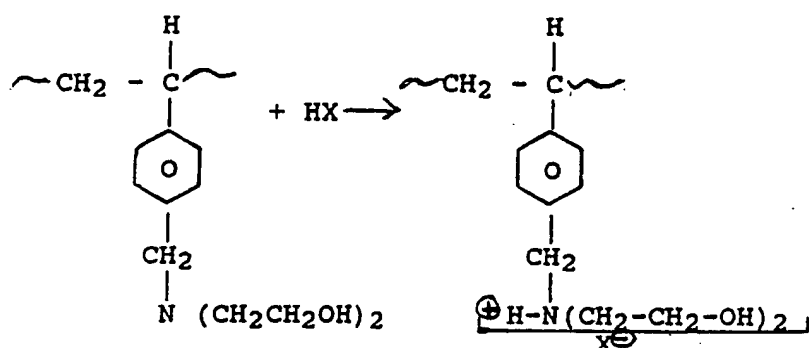
Under the conditions of this reaction in the presence of a high stoichiometric excess of diethanol amine, most of the HBr formed in the nucleophilic substitution reaction is complexed with unreacted diethanol amine and is removed during work-up so that the major product is the benzylic iminodiethanol as shown. (Some of the remaining bromine may be present as the hydrobromide complex with the pendant imino-diethanol functionality but the level is too low to make it act as an ionomer.) The attached 1' hydroxy functionality makes this pendant functionalized polymer reactive with isocyanates, carboxylic acids, epoxides, etc., so that it is useful in polyurethanes, polyesters, epoxy resins, etc. The attached hydroxy groups also make the polymer hydrophilic and self-emulsifying to some degree and impart dispersant activity. As shown below, this pendant functionalized polymer readily forms acid adducts to become an ionomer with many of the properties of the other cationic ionomers of Examples 1-3.

In order to form the acid adducts, 10 g. of this dried pendant functionalized polymer was dissolved in 90 g. of hexane to yield a 10% solution and this was shaken in a separatory funnel with an aqueous phase made up of 1 g. of concentrated hydrochloric acid (37%), 89 g. of water and 10 g of isopropanol. The shaking produced a stiff, gel-like water-in-oil paste from which the polymer was recovered by precipitating and kneading in isopropanol. The polymer was further purified by kneading in a 50/50 water/methanol mixture and then vacuum-oven dried at 70°C with 0.2 wt.% BHT mixed in as an antioxidant. The recovered dried polymer was now an extremely tough ionomerically

- 109 -

cross-linked elastomer. It was now insoluble in hexane or other hydrocarbons, but readily soluble in an hexane/isopropanol blend which was able to disrupt the ionic cross-link by solvation.

The HBr acid adduct was prepared in exactly the same way by substituting 1 g. of concentrated hydrobromic acid for the hydrochloric acid and the recovered HBr adduct was again a very tough ionomerically cross-linked elastomer. Other acid adducts could be prepared in similar fashion by using the desired acid. The reaction and analyses are shown below:



Analysis

	Pendant Functionalized		
	Polymer	HCl Adduct	HBr Adduct
M_v	~130,000	~130,000	~130,000
Wt.% Br	0.2	0.2	1.49
Wt.% Cl	-	0.48	-
Wt.% N	0.28	0.28	0.28

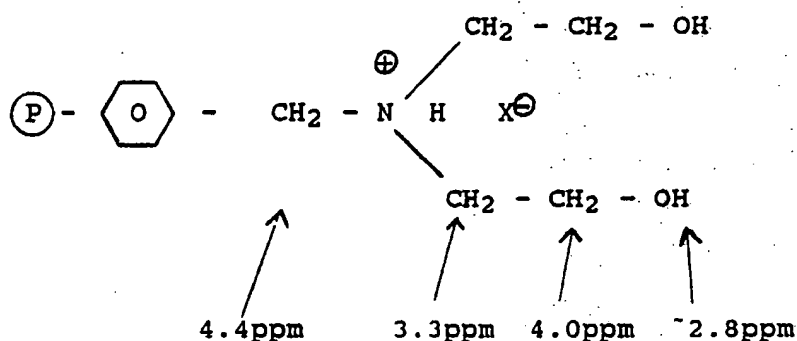
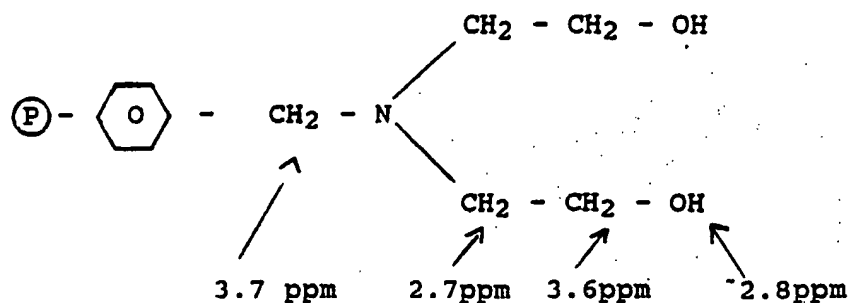
The proton NMR spectra showed the appropriate resonances which by integration confirmed the

- 110 -

chemical analyses in showing first the complete conversion of benzylic bromines to iminodiethanol functionality and then the nearly complete conversion of the pendant functionality to the acid adducts.

- 111 -

Proton NMR Resonances for Enchained Pendant Functional "mer" Units



As indicated the acid adducts have resonances for the benzylic protons and the methylene protons adjacent to the nitrogen which are nearly as far upfield as for the similar protons in the quaternary ammonium salts of example 2A confirming the strongly ionic nature of the acid adducts. These acid adducts are readily converted to self-emulsifying cationic latexes as for the other ionomers of examples 1-3, but also contain primary hydroxy functionality which impacts new reactivity and extends utility into still

- 112 -

other applications. Clearly the iminodiethanol pendant functionality imports versatile and useful properties.

It is also obvious that one skilled in the art could use other secondary amines containing other functional R groups as the nucleophilic reagent in place of the diethanol amine of this example to prepare pendant functionalized polymers with other functionality attached to the benzylic position of the "base" terpolymer by means of the amine nitrogen nucleophile, and that these could be converted to acid adduct ionomers as desired. Thus, iminodiacetic acid could be used in place of diethanol amine to attach pendant carboxylic acid groups or iminodiacetonitrile could be used to attach pendant nitrile groups, etc. It is also obvious that tertiary amines containing functional R groups could be used to attach pendant quaternary ammonium salt groups containing the other functionality in the R groups.

4B

In this example, pendant hydroxy functionality was attached to a random isobutylene/para-methylstyrene/para-bromomethylstyrene "base" terpolymer by nucleophilic substitution using diethanol amine as the nucleophilic reagent, but because the sequential nucleophilic substitution reaction involving already attached pendant iminodiethanol as a nucleophilic reagent was not controlled a cross-linked "gelled" polymer of diminished utility resulted. The "base" terpolymer used in this example was identical to that used in Example 4A and contained 0.9+ mole %

- 113 -

para-bromomethylstyrene, 1.4 mole % paramethylstyrene, and 97.7 mole % isobutylene with a viscosity average molecular weight of 135,000.

In the nucleophilic substitution reaction; 750 g. of the "base" terpolymer were dissolved in 2438 g of B & J hexane in a 5 l resin flask with stirring under nitrogen to form a 23.5% solution by weight. Then 33.5 g of diethanol amine (~ 2 moles/mole bromine) in 610 g of isopropanol was added slowly with stirring at room temperature to give a 19.7 wt.% polymer solution in an 80/20 hexane/isopropanol solvent blend with 2 moles/mole of bromine of the diethanol amine nucleophilic reagent. The solution was allowed to stir at room temperature for two hours and then heated with stirring under N_2 to reflux at 63°C. It was stirred at reflux for 7 hours before being cooled with samples being taken after various times to monitor the progress of the reaction. As in Example 4A, all the samples emulsified when shaken with water forming stable emulsions which could not be separated by any technique tried so that it was not possible to wash them before recovery by precipitation and kneading in isopropanol. As in the previous example then it was necessary to remove unreacted diethanol amine and further purify the recovered polymer by extensive kneading in isopropanol and then further kneading in a 50/50 water/methanol mixture before vacuum oven drying @ 70°C with 0.2 wt.% BHT mixed in as an antioxidant.

In this example though, all the samples and the final product were cross-linked after oven drying. They were completely insoluble and intractable so that characterization was difficult. The

- 114 -

final recovered polymer was in each case a tannish cross-linked tough sponge rubber which was not only insoluble, but also could not be caused to flow in order to be formed into test specimens even in a hot press. The extent of cross-linking appeared to diminish somewhat (as judged by the force required to stretch the dried spongy rubber and by the extent of swell in solvents) as reaction time increased, but even the final sample after 7 hours of reflux was still insoluble despite the fact that the nucleophilic substitution reaction had nearly gone to completion as judged by elemental analyses for bromine loss and nitrogen content (spectral analyses were not possible because of sample intractability).

Elemental Analyses on Samples

<u>Sample</u>	<u>Reaction Time @ Reflux</u>	<u>Wt.% Br</u>	<u>Wt.% N</u>
Orig "BASE" Poly	-	1.6	0
A	several minutes	0.8	.14
B	1 hour	0.48	.27
C	3 hours	0.38	.25
Final	7 hours	0.28	.28

The elemental analyses on sample A taken just after reflux temperature was reached suggest that the nucleophilic substitution reaction was already about 50% complete. The polymer appeared to be "gel free" during work-up, but was a very tightly cross-linked spongy mass after vacuum - oven drying. The elemental analyses suggest that the substitution reaction had gone nearly to completion in the remaining

- 115 -

samples, with the residual bromine content of the final rubber being as low as that in the soluble product of Example 4A, but nevertheless all were cross-linked and insoluble. In fact, they appeared to be already gelled during work-up and prior to vacuum oven drying.

It is apparent that under these reaction conditions the sequential reaction involving already attached iminodiethanol functionality reacting with remaining benzylic bromine to form quaternary ammonium cross-links is proceeding fast enough to always yield an undesirable gelled (insoluble) pendant functionalized polymer. If the reaction is stopped at an early stage, cross-linking occurs during drying; if the reaction is allowed to proceed more nearly to completion; the cross-linking occurs competitively with the desired nucleophilic substitution reaction. In order to produce the desired soluble pendant functionalized polymer, it is necessary to speed up the desired substitution reaction and/or retard the undesired sequential reaction. This was achieved in Example 4A by using a larger stoichiometric excess of the diethanol amine nucleophilic reagent and by using a solvent system and reaction temperature which speeded up the desired reaction to drive it to completion before the sequential reaction became important.

This example shows the necessity for considering the consequences of possible sequential reactions and of choosing reaction conditions to avoid them in order to produce the desired soluble pendant functionalized polymers of this invention.

- 116 -

The use of functional group containing amines as the nucleophilic reagent for reaction with the para-bromomethylstyrene containing "base" terpolymers of the invention is a general method for attaching pendant functionality such as hydroxy, carboxy, nitrite etc. - but it must always be used with careful recognition and control of the sequential and competing nucleophilic substitution reactions in order to avoid cross-linking and produce the desired soluble pendant functionalized polymers of this invention.

Another way of introducing pendant hydroxy functionality is via esterification and hydrolysis as taught in Example 6.

Example 5

Preparation of Pendant Functionalized Iso-butylene/Paramethyl Styrene Copolymer Containing Dithiocarbamate Ester functionality

5A

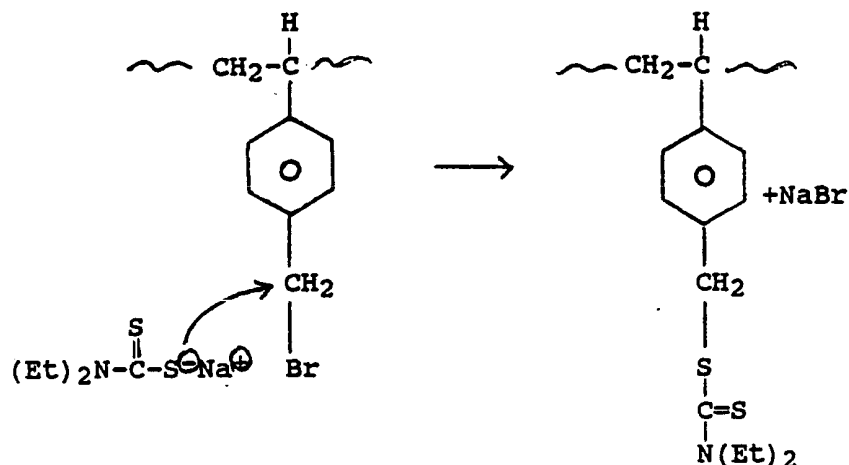
In this example, pendant dithiocarbamate ester functionality was attached to a random isobutylene/paramethylstyrene/paramethyl brominated para-bromomethylstyrene "base" terpolymer by nucleophilic substitution using sodium diethyl dithiocarbamate as the nucleophilic reagent. The "base" terpolymer containing the reactive electrophilic benzylic bromines was prepared as already outlined. The starting copolymer was the same as used in Example 1A; it contained 6.6 wt.% paramethylstyrene with a viscosity average molecular weight of 68,000. It was

- 117 -

radically brominated using light initiation at 40°C as a 15% solution in hexane to give a "base" terpolymer with a viscosity average molecular weight of 65,000 and containing 4.3 wt.% bromine. The "base" terpolymer composition was 96.70 mole % isobutylene, 2.60 mole % para-bromomethylstyrene, and 0.7 mole % paramethylstyrene. There was some dibrominated paramethylstyrene present because of the high bromination level achieved. In the nucleophilic substitution reaction; 200g of the "base" terpolymer was dissolved in 2100 g of toluene in a 5 l resin flask under nitrogen to form an 8.7 wt.% solution. Then 22 g. of sodium diethyl dithiocarbamate dissolved in 700 g of isopropyl alcohol was added slowly with stirring at room temperature to give a 6.6% polymer solution in an 75/25 toluene/isopropanol solvent blend with 1.2 moles per mole of Br of the nucleophilic reagent. The solution was heated with stirring under N₂ to 80°C and stirred @ 80°C for 6 hours to complete the nucleophilic substitution reaction before being cooled - however, samples removed after 1 and 3 hours showed that the reaction was already over after 1 hours @ 80°C. The cooled solution was given several water washes to remove the sodium bromide byproduct and other water solubles and then the polymer was removed by precipitation and kneading in isopropanol as in the earlier examples. The dried polymer was recovered by vacuum oven drying at 70°C without added stabilizers since the attached dithiocarbamate ester groups themselves acted as a polymer bound stabilizer. The recovered polymer was a tough slightly tannish elastomer with complete solubility in hexane. Analyses as summarized below showed a very high conversion of

- 118 -

benzylic bromine to dithiocarbamate ester had been achieved:

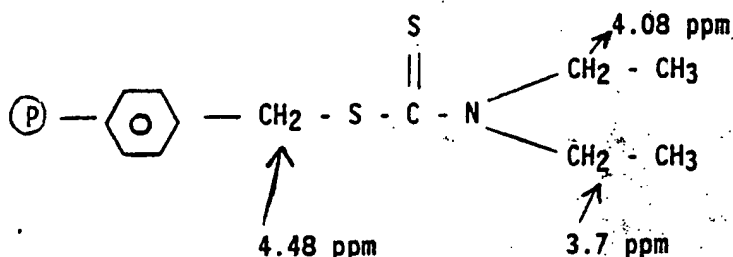


Analyses

	<u>"base" terpolymer</u>	<u>pendant functionalized polymer</u>
Mv	65,000	65,000
wt.% Br	4.3	0.6
wt.% sulfur	-	2.97
wt.% N	-	0.65
	<u>NMR</u>	
mole % benzylic Br	2.6	-
mole % dithiocarbamate ester	-	2.6

The proton NMR spectra confirmed the chemical analyses in showing the quantitative conversion of benzylic bromine functionality to pendant dithiocarbamate ester functionality.

Proton NMR Resonances for Enchained

Pendant Functional Dithiocarbamate Ester "Mer" Unit

This experiment shows that facile conversion of benzylic bromine functionality in the "base" polymer to pendant dithiocarbamate ester functionality is possible via nucleophilic displacement. The attached dithiocarbamate ester functionality provides built-in antioxidant protection to the polymer as well as vulcanization and covulcanization activity and permits free radical chemistry to be employed as is discussed more later.

5B

In this example a "base" isobutylene/para-methylstyrene/para-bromomethylstyrene terpolymer was prepared and converted via a sequential reaction route to a copolymer containing pendant dithiocarbamate ester functionality without separate isolation and recovery of the intermediate "base" terpolymer. This sequential reaction route which avoids recovery of the intermediate "base" copolymer is of course economically advantageous.

An isobutylene/paramethylstyrene random copolymer containing 4.8 wt.% paramethylstyrene with a Mooney viscosity of 30 (the same copolymer used in

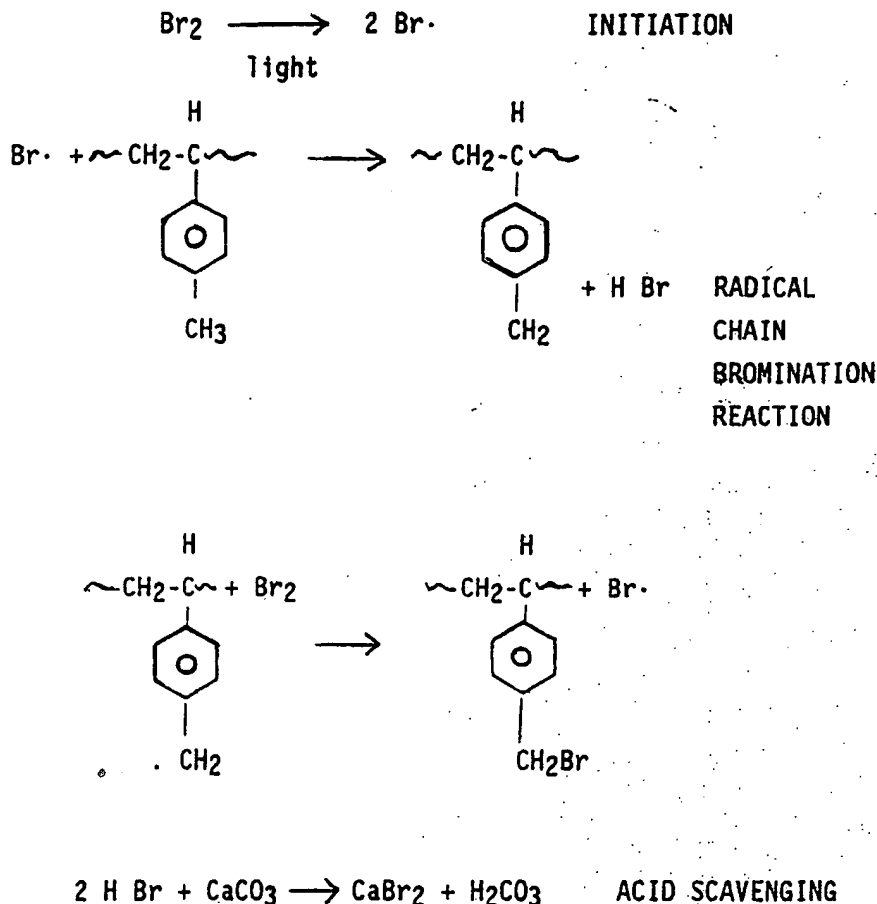
- 120 -

Example 2A) was dissolved in hexane under nitrogen to form a 17 wt.% solution with 8% by wt. of atomite CaCO_3 stirred in suspension as an acid scavenger to give an opaque white slightly viscous solution which was heated with stirring under nitrogen to 60°C. The solution was illuminated with a 120 Watt Spotlight and then with continued stirring @ 60°C with slight nitrogen purge, 6.5 wt.% bromine on polymer was added as a 20% solution in hexane. The solution turned bright orange/red as the bromine was added but the color rapidly faded as the radical bromination reaction took place. Despite the opacity of the solution, the light-initiated bromination progressed rapidly so that the bromine cooler had completely discharged and the light was turned off within 5 minutes. A sample of the brominated solution was removed to enable characterization of the brominated "base" terpolymer and then 1 mole of sodium diethyl dithiocarbamate per mole of bromine was added as a 5% solution in isopropanol to give an 80/20 hexane/isopropanol solvent blend and the solution was stirred hot @ 60°C to effect the nucleophilic substitution reaction. Samples removed at 15 minute intervals to follow the progress of the reaction showed that it was complete within 1/2 hour. The samples and final solutions were given several water washes with dilute HCl (1%) to convert excess CaCO_3 to CaCl_2 and remove it and other water solubles into the aqueous wash and then given several water washes to remove traces of acid before the polymer was recovered by precipitation and kneading in isopropanol as in the earlier examples.

In the first step of this sequential reaction, a portion of the enchaind paramethylstyrene

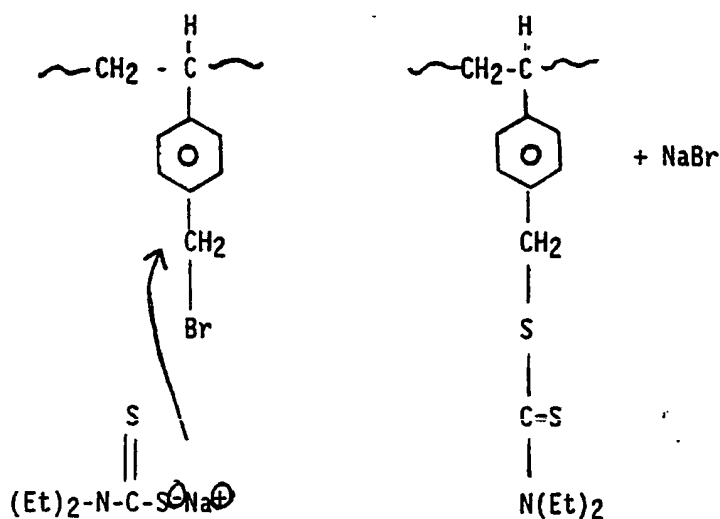
- 121 -

moieties of the starting copolymer were converted to para-bromomethylstyrene moieties by light initiated radical bromination with the byproduct HBr being removed by reaction with the dispersed calcium carbonate:



In the second step of the sequential reaction, the sodium diethyl dithiocarbamate nucleophilic reagent reacted with the electrophilic benzylic bromines to produce the desired pendant functionalized product:

- 122 -



Analyses as summarized below showed that the intermediate "base" terpolymer contained 1.2 mole % benzylic bromine functionality whereas the final pendant functionalized product contained 0.9 mole % dithiocarbamate ester pendant functionality with 0.3 mole % benzylic bromine functionality remaining.

- 123 -

Analyses

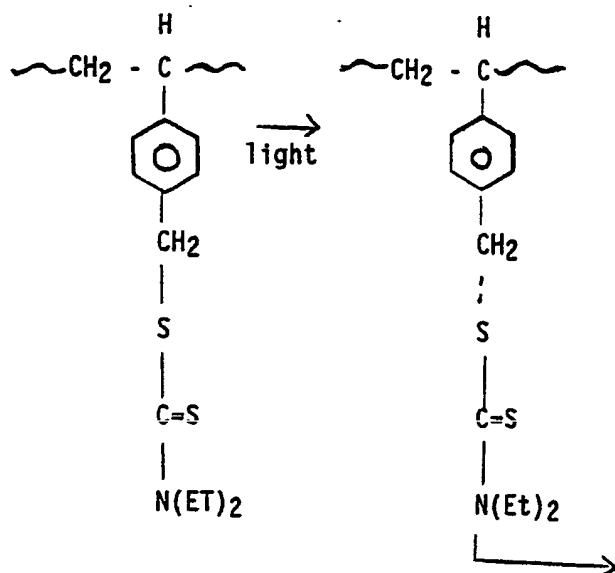
	Starting	Intermediate	Final pendant
	<u>Copolymer</u>	<u>"base" Terpolymer</u>	<u>Functionalized product</u>
Mv	- 280,000	280,000	280,000
wt% Br	- -	2.0	0.5
wt% S	- -	-	1.0
wt% N	- -	-	0.2

NMR

mole % PMS	- 2.3	1.1	1.1
mole % Br PMS	- -	1.2	0.3
mole % dithio- carbamate ester	- -	-	0.9

This mixed functionality polymer was stable without any added antioxidants and was vulcanizable with promoted zinc oxide and/or conventional sulfur vulcanization systems. It also showed good covulcanization in blends with natural rubber. Films of this copolymer cross-linked on exposure to U.V. irradiation as opposed to the degradation normally experienced with high isobutylene containing polymers under U.V. irradiation. This cross-linking under irradiation is attributed to the ready ability of the dithiocarbamate ester functionality to form stable radicals under irradiation to permit radical cross-linking and other radical chemistry reactions to occur rather than backbone cleavage as normally occurs with isobutylene based polymers:

- 124 -



cross-links by coupling insertion reactions, etc.

This ability of the dithiocarbamate ester functionality to prevent U.V. degradation and/or to impart controlled cross-linking under free radical conditions is very valuable in exterior applications such as roofing, coating, white tire sidewalls, etc., where the tendency of isobutylene base copolymers to degrade and develop surface tackiness has always impaired their utility in such areas.

5C

In this example a pendant functionalized isobutylene based polymer containing nearly equal amounts of dithiocarbamate ester and benzylic bromine functionality was prepared via a sequential reaction route without recovery of the intermediate "base" terpolymer.

- 125 -

Five hundred grams of an isobutylene/-paramethyl styrene random copolymer containing 4.5 mole % paramethyl styrene with a Mooney viscosity of 34 was dissolved in 2833 grams of n-hexane under nitrogen in a 5 l resin flask to yield a 15 wt.% solution. Forty-five grams of Omyacorb UFT calcium carbonate was stirred in as an acid scavenger to yield an opaque white dispersion and then the solution was heated with stirring to 60°C and illuminated with a 120 Watt spotlight. Thirty-five grams of bromine (7 wt.% on polymer) was added as a 25 wt.% solution in hexane to effect radical bromination and produce the "base" terpolymer. The bromination reaction was over in <5 minutes and after removal of a sample for characterization of the "base" terpolymer, 30 grams of sodium diethyl dithiocarbamate (~ 0.9) moles/mole of bromine) dissolved in 600 grams of isopropanol (to give on 83/17 hexane/isopropanol solvent blend) was added to effect the nucleophilic substitution reaction and the solution was stirred at 60°C for 1/2 hour to complete the reaction. The solution was cooled and acid washed and then the polymer recovered by alcohol precipitation as in example 5B. The sequential reactions proceeded as already outlined. Analyses as summarized below showed on intermediate "base" polymer with 2.2 wt.% bromine and a final pendant mixed functionalized product with 0.7 mole % benzylic bromine and 0.7 mole % dithiocarbamate ester functionality.

- 126 -

Analyses

	<u>Starting Copolymer</u>	<u>Intermediate "Base" Terpolymer</u>	<u>Final Mixed Pendant Functionalized Product</u>
Mooney	- 34	33.5	33
Wt% Br	- \	2.2	1.05
Wt% S	- \	\	0.77
Wt% N	- \	\	0.17

NMR

Mole% PMS	- 4.5	3.1	3.1
Mole% Br PMS	- \	1.4	0.7
Mole% Dithiocarbamate Ester	- \	-	0.7

These examples show that pendant dithiocarbamate ester functionality is readily introduced into the "base" terpolymer of this invention by a nucleophilic substitution reaction; stable mixed functionality polymers containing both benzylic bromine and dithiocarbamate ester functionality can be made at any desired ratio of the functionalities; and that an economical sequential reaction route can be utilized.

Example 6

Preparation of Pendant Functionalized Isobutylene/Para-methylStyrene Copolymer Containing Various Ester Functionalities

6A

In this example pendant cinnamate ester functionality was attached to a random

- 127 -

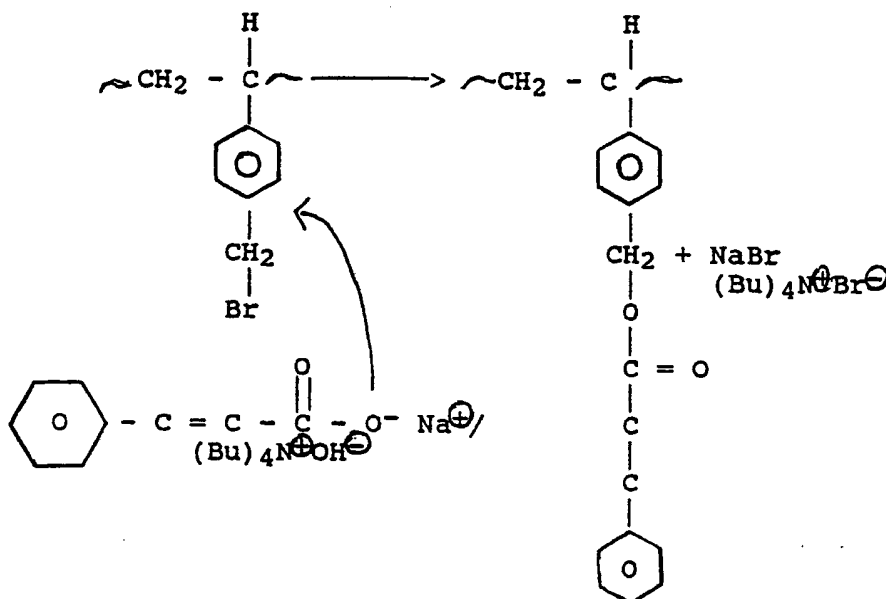
isobutylene/paramethyl styrene/para-bromomethylstyrene "base" terpolymer by nucleophilic substitution using a cinnamic acid salt as the nucleophilic reagent. The "base" terpolymer used in this example was identical to that used in examples 4A and 4B and contained 0.9 mole% paramethyl brominated paramethyl styrene, 1.4 mole% paramethyl styrene, and 97.7 mole% isobutylene with a viscosity average molecular weight of 135,000.

In the nucleophilic substitution reaction, 750 g of the "base" terpolymer was dissolved in 3000 g of toluene in a 5 l resin flask by stirring under N₂ to form a 20 wt% solution. Then 35.4 g of cinnamic acid (1.5 moles/mole bromine); 77.3 g 40% tetrabutyl ammonium hydroxide (0.5 mole/mole acid) and 9.6 g 50% sodium hydroxide (0.5 mole/mole acid) were stirred in and the resulting emulsion was heated to reflux at 86°C with stirring and with an air condenser attached. The solution was refluxed for 3 hours at 86°C to complete the reaction with samples removed at reflux and after one half and one and one half hours of reflux to monitor the progress of the reaction. The solution gradually became clearer during reaction and after three hours was a translucent, light beige color. The final solution and samples were given acidic, basic, and neutral washes and then the polymer was recovered by precipitation and kneading in isopropanol as in earlier examples and then vacuum oven drying at 70°C with a 0.2 wt% BHT mixed in as an antioxidant. Analyses as summarized below show that the nucleophilic substitution reaction was proceeding slowly and had still not gone to completion after three hours of reflux:

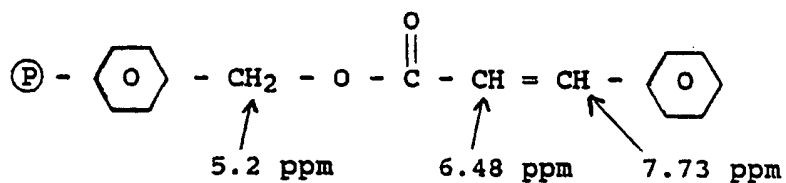
- 128 -

	<u>Wt% Bromine</u>
Starting Base Terpolymer	- 1.60
@ Reflux	- 1.37
1/2 Hour Later	- 1.08
1 1/2 Hours Later	- 0.91
(Final) 3 Hours Later	- 0.54

The final product after three hours of re-flux contained 0.8 mole% cinnamate ester with only 0.1 mole% benzylic bromine left so the nucleophilic substitution reaction had gone nearly 90% to completion:



Proton NMR spectra was used to quantify the amount of cinnamate ester functionality introduced:



- 129 -

with of course the new aromatic protons also being present in the spectra.

This experiment shows that pendant carboxylic acid ester functionality can be introduced into the "base" polymer of this invention by nucleophilic substitution under suitable conditions. The cinnamate ester functionality is interesting in that it enables cross-linking to occur when the polymer is irradiated under suitable conditions.

6B

In this example, pendant fatty acid ester functionality was attached to a random isobutylene/paramethyl styrene/para-bromomethylstyrene "base" terpolymer by nucleophilic substitution using a commercial C₁₈ fatty acid high in linolenic acid (Industrene 120 from Witco Corporation) as the fatty acid. The "base" terpolymer used had a Mooney viscosity of 30 and contained 2.0 mole% para-bromomethylstyrene, 5.0 mole% paramethyl styrene, and 93.0 mole% isobutylene.

In the nucleophilic substitution reaction, 500 g of the "base" terpolymer was dissolved in 2833 g of toluene in a 5 l resin flask under nitrogen to form a 15 wt% solution. Then 63.3 g of Industrene 120 Linseed fatty acid (1.2 moles/mole Br) was added along with 72.8 g of 40% tetrabutyl ammonium hydroxide (0.5 moles/mole acid) and 9.0 g 50% NaOH (0.5 moles/mole acid) to form an opaque, slightly yellowish emulsion which was heated with stirring to reflux at $\wedge 87^{\circ}\text{C}$ under nitrogen with an air condenser attached. The emulsion was refluxed for two hours before being

- 130 -

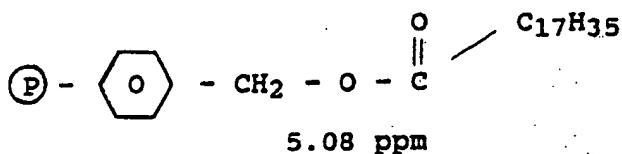
cooled with samples being removed at reflux, after one half hour and after one hour of reflux to monitor the progress of the reaction. During the reaction the solution became clearer with water droplets being distilled over into the condenser. The final solution was a translucent, light yellow color. The samples and final solution were given acidic, basic, and then neutral water washes before being precipitated in isopropanol and vacuum oven dried as usual. Analyses as shown below indicate that the nucleophilic substitution with the C₁₈ fatty acid was faster than with the cinnamic acid and was essentially done in one hour -- apparently the carboxylate nucleophile attached to the C₁₇ hydrocarbon achieves intimate contact with the benzylic bromine electrophile attached to the "base" terpolymer more easily than when the carboxylate is attached to a shorter alkyl group.

	<u>Wt% Bromine</u>
Starting Base Terpolymer	- 3.0
@ Reflux	- 1.06
1/2 Hour Later	- 0.45
1 Hour Later	- 0.29
(Final) 2 Hours Later	- 0.23

NMR analyses, as depicted in Figure 1, showed the final product contained 2.0 mole% ester and essentially no benzylic bromine indicating that the nucleophilic substitution reaction had gone to completion. (The small residual bromine content as measured by a Princeton-Gamma Tech Bromine Analyzer probably represents inorganic bromides not fully washed out during recovery). The NMR spectra (attached) shows a resonance due to the benzylic ester protons at 5.08

- 131 -

ppm and a broad complicated resonance due to the olefinic protons in the C₁₈ chain at 5.3-5.5 ppm.



(The benzylic ester protons of the cinnamate ester of example 6A showed a higher field resonance at 5.2 ppm due to the conjugation present in the cinnamate ester.)

The fully converted linseed oil acid ester derivative of this example showed no evidences of cross-linking and remained completely soluble when compounded and heated under typical vulcanization conditions with zinc oxide or promoted zinc oxide vulcanization systems which are effective with the starting brominated "base" terpolymer (confirming the absence of any remaining benzylic bromines), but gave good vulcanizates when compounded and cured with typical sulfur vulcanization systems such as:

Polymer	- 100
Sulfur	- 1.25
M. Tufts	- 1.50
Altax	- 1.0
Zinc Oxide	- 3.0

The presence of unsaturation in the pendant fatty acid side chains thus permits conventional sulfur vulcanization systems to be employed to vulcanize the functionalized ester derivative of this example. The pendant unsaturation is also useful in permitting co-vulcanization with the high unsaturation general purpose rubbers such as natural rubber or SBR. Testing

- 132 -

of sulfur vulcanized test specimens of this ester derivative in a standard ozone resistance test showed that they retained the outstanding ozone resistance characteristic of the saturated "base" terpolymer vulcanizates. The pendant unsaturation in the side chain thus imparts conventional sulfur vulcanization activity without adversely affecting ozone resistance.

6C

In this example an attempt to attach pendant fatty acid ester functionality to a random isobutylene/paramethylstyrene/para-bromomethylstyrene "base" terpolymer by nucleophilic substitution was unsuccessful because the key requirements as taught in this patent were not followed. The fatty acid used in this example was the same linseed oil acid (Industrene 120) used in example 6B. The "base" terpolymer used had a Mooney viscosity of 30 and contained 0.75 mole% para-bromomethylstyrene, 1.6 mole% paramethylstyrene and 97.65 mole% isobutylene.

In the attempted nucleophilic substitution reaction, 200 g of the "base" terpolymer was dissolved in 1133 g of toluene in a 2 l resin flask under nitrogen purge to form a 15% solution to which 15 g of Industrene 120 (\approx 1.7 moles/mole of bromine) and 3.0 g calcium oxide powder (1 mole/mole acid) was added. The reaction mixture was then heated to 90°C and stirred hot for eight hours before being cooled, with samples being removed periodically to monitor the progress of the reaction. No reaction occurred -- The polymer recovered from the samples and the final product was identical to the starting "base" terpolymer. It showed no bromine loss or ester formation.

The nucleophilic substitution reaction did not proceed because the required, intimate contact between the nucleophilic reagent and the polymeric electrophile was not achieved under the proper solvation conditions. The ionic calcium carboxylate soap

- 134 -

will not react at an appreciable rate with the polymeric benzylic bromine in toluene solution at these temperatures.

Reactions under similar conditions with sodium hydroxide, potassium hydroxide, or ammonium hydroxide used in place of the calcium oxide also failed to proceed for the same reason; but when intimate contact is achieved under the proper solvation conditions and temperature, then the desired "clean" nucleophilic substitution proceeds rapidly as in examples 6A and 6B with some tetrabutyl ammonium hydroxide present. Successful substitution is also achieved when 18 -Crown- 6 is used in conjunction with KOH to solvate the mixture site or when other proper solvating phase transfer catalysts are used.

6D

In this example an attempt to produce a soluble pendant fatty acid ester functionalized polymer failed because a competing reaction which produced cross-links was not controlled and a gelled product of limited utility resulted. As in the previous examples, Industrene 120 was used as the fatty acid while the "base" terpolymer was a random isobutylene/paramethylstyrene/para-bromomethylstyrene terpolymer with a viscosity average molecular weight of 285,000 and containing 4.2 mole% para-bromomethylstyrene, 4.0 mole% paramethylstyrene and 91.8 mole% isobutylene.

In the nucleophilic substitution reaction, 200 g of the "base" terpolymer was dissolved in 1133 g of toluene to give a 15% solution to which 36 g of

- 135 -

Industrene 120 (0.75 moles/mole bromine), 2.5 g 40% tetrabutyl ammonium hydroxide (0.1 moles/mole acid) and 8 g 28% ammonium hydroxide (0.5 moles/mole acid) were added before heating to 90°C to initiate the substitution reaction. As the reaction mixture was heated, it thickened and, shortly after reaching 90°C, it totally gelled. The recovered polymer was a tough, insoluble gel and could not be characterized.

In this instance, at a relatively low level of the onium salt, the esterification reaction was proceeding slowly and the competing N-alkylation reaction with the ammonium salt was occurring rapidly enough to produce a cross-linked gel of limited utility.

These negative examples show that the key requirements as taught in this invention must be observed in order to produce the desired soluble pendant functionalized polymers of this invention.

6E

In this example, pendant fatty acid ester functionality in which the fatty acid contained conjugated unsaturation was attached to the "base" terpolymer. The fatty acid used was derived from Tung oil and was high in eleostearic acid. The "base" terpolymer had a Mooney viscosity of 32 and contained 3.6 wt% bromine. It was a terpolymer containing 2.2 mole% para-bromomethylstyrene, 2.7 mole% paramethylstyrene, and 95.1 mole% isobutylene. In the nucleophilic substitution reaction, 666 g of "wet" base terpolymer crumb (✓500 g dry weight) were dissolved

- 136 -

in 2833 g toluene in a 5 l resin flask to yield a 15% polymer solution containing dispersed water. This use of "wet" crumb in the nucleophilic substitution reaction is advantageous as it avoids the need to finish the brominated "base" terpolymer prior to converting it to the pendant functionalized polymer. To the "wet" polymer solution were added: 76 g of Tung oil acid (~ 1.2 moles/mole bromine), 87.4 g 40% tetrabutyl ammonium hydroxide (0.5 moles/mole acid) and 43 g 50% sodium hydroxide (0.2 moles/mole acid) to give a milky white emulsion which was heated to reflux at about 84°C with an air condenser attached. The reaction mixture was stirred hot at reflux for one hour before being cooled and washed and recovered as previously outlined. Samples removed at reflux and one half hour later were similarly recovered.

The substitution reaction was proceeding rapidly under these conditions as shown by the following bromine analyses:

	<u>Wt% Bromine</u>
Starting Base Terpolymer	- 3.6
@ Reflux	- 0.78
1/2 Hour Later	- 0.56
(Final) 1 Hour Later	- 0.40

The NMR spectra, as depicted in Figure 2, shows a resonance due to the benzylic ester protons at 5.08 ppm, some residual resonance of 4.47 ppm due to remaining benzylic bromide, and a series of resonances at 5.3-6.4 ppm due to the olefinic protons of the C₁₈ acid (with the conjugated unsaturation resonances being the high field resonances at >5.9 ppm). The final product contained 1.9 mole% ester with 0.2 mole%

- 137 -

benzylic bromide remaining. It was completely soluble with a Mooney viscosity of 31, the same as the starting "base" terpolymer.

Despite the highly active nature of the pendant conjugated unsaturation, this functionalized polymer showed good stability with no tendency to cross-link during drying or storage. However, the attached conjugated unsaturation permitted facile vulcanization and covulcanization with unsaturated rubbers with sulfur vulcanization systems. The conjugated unsaturation also provided good cross-linking under electron beam irradiation and permitted oxidative surface curing to occur upon outdoor exposure to sunlight -- a highly useful property in exterior coatings such as roof coatings. The conjugated unsaturation is also very active in radical reactions to permit grafting reactions with free radical polymerizable monomers. This highly active Tung acid ester derivative is thus useful in a wide range of applications.

It is obvious that nucleophilic substitution reactions with various carboxylic acids could be used to attach many other functional side chains such as hydroxy using ricinoleic acid, etc.

6F

In these examples pendant acrylate functionality was attached to the "base" terpolymer via esterification with acrylic or methacrylic acids. The pendant acrylate side chain produces cross-linkability under irradiation and permits grafting reactions with free radical polymerizable monomers. The "base"

- 138 -

terpolymers used in these reactions were isobutylene/paramethyl styrene/para-bromomethylstyrene terpolymers. They are characterized in the examples in terms of the weight present of electrophilic /para-bromomethylstyrene present.

Example 6F-1: Reaction of
Poly(isobutylene-co-para-bromomethylstyrene-co
para-methylstyrene with Methacrylic Acid.

A 1 liter glass reaction vessel, fitted with a magnetic stirrer, a hose connector, and a septum was purged with nitrogen. Operating in an atmosphere of nitrogen, the vessel was charged with a cyclohexane solution (500 ml) which contained 50 grams poly(isobutylene-co-para-bromomethylstyrene) ($M_v = 10k$, 4.6% para-bromomethylstyrene). A cyclohexane solution of tetrabutylammonium 2,6-di(t-butyl)-4-methylphenoxide was prepared in a second flask under nitrogen by placing 100 ml cyclohexane, 30 ml tetrabutylammonium hydroxide (1 M in methanol) and 6.6 g 2,6-di(t-butyl)-4-methylphenol into the flask and concentrating this solution down to half its volume. This solution was then added to the flask containing the poly(isobutylene-co-para-bromomethylstyrene). Then 2.5 ml methacrylic acid was added to the polymer solution and the temperature of the solution was raised to 50°C. The reaction was complete in one hour and the polymer was isolated by precipitation in isopropanol. The polymer was dried in a vacuum oven at 1 mm Hg and 40°C. GPC of the recovered polymer (50 g, 100% yield) was identical to that of the starting poly(isobutylene-co-para-bromomethylstyrene). The analysis for the methacrylate content (FTIR and NMR) indicate

- 139 -

that the modified polymer had 0.58 meq/gram which is consistent with the complete conversion of methacrylic acid to methacrylic ester.

Example 6F-2: Reaction of
Poly(isobutylene-co-para-bromomethylstyrene-co-
paramethylstyrene) with Acrylic Acid

A 5 liter glass reaction vessel, fitted with a magnetic stirrer, a hose connector, and a septum were purged with nitrogen. Operating in an atmosphere of nitrogen, 297 grams of poly(isobutylene-co-para-bromomethylstyrene) ($M_v = 1.2M$, 1.7% para-bromomethylstyrene) was placed into the vessel along with 3.5 liters of xylenes. The polymer was dissolved with stirring under a partial vacuum of 100 mm Hg with a nitrogen sparge attached at the bottom of the solution. A xylene solution of tetrabutylammonium acrylate was prepared in a second flask under nitrogen by placing 100 ml xylenes, 60 ml tetrabutylammonium hydroxide (1 M in methanol) and 6.0 g acrylic acid together with stirring. The contents of the flask was concentrated to half its volume and then diluted to 0.5 liters with more xylenes. This solution was then added to the flask containing the poly(isobutylene-co-para-bromomethylstyrene) and the temperature of the solution was raised to 65°C. The reaction was complete in six hours and the polymer was isolated by precipitation in isopropanol. The polymer was dried in a vacuum oven at 1 mm Hg, 40°C. The analysis for the acrylate content (FTIR and NMR) indicate that the modified polymer has 0.24 meq/gram which is consistent with the complete conversion of acrylic acid to

acrylic ester and total conversion of the benzyl-bromide.

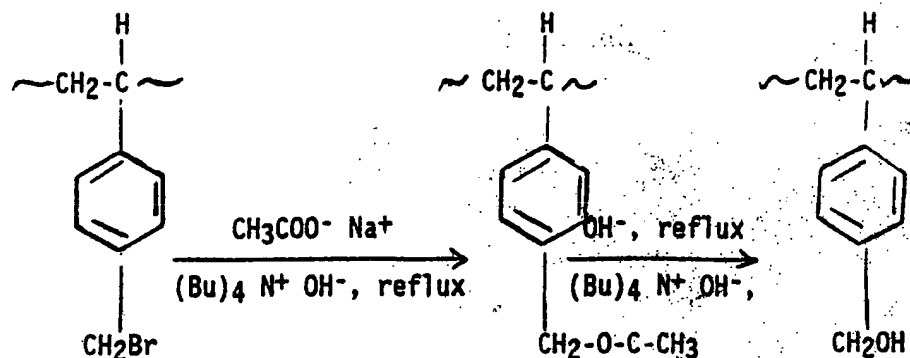
These examples again show that by observing the key requirements as taught in this invention nucleophilic substitution using a carboxylate nucleophile can be used to attach highly useful pendant functionality via an ester linkage.

Example 7

Preparation of Pendant Functionalized Isobutylene/Paramethyl Styrene Copolymer Containing Hydroxy or Mixed Ester and Hydroxy Functionalities

In these examples, pendant acetate ester functionality was attached to a random isobutylene/paramethyl styrene/para-bromomethylstyrene "base" terpolymer by nucleophilic substitution using an acetic acid salt as the nucleophilic reagent and then in a sequential reaction all or some part of the ester functionality was hydrolyzed to introduce pendant hydroxy functionality. In this way, pendant functionalized polymers containing benzylic bromine, ester, and hydroxy pendant functionality in any desired ratio can be produced. These saturated, functionalized polymers can be used in conjunction with and coreacted with many other functional resins as tougheners, impact modifiers, etc. They open up the vast areas of urethane, epoxy, etc. chemistry to these isobutylene-based polymers.

The sequential reaction sequence as shown:



is in essence an hydrolysis of the bromomethyl group with hydroxy ion as the nucleophile.

The brominated "base" terpolymer chosen for these studies was brominated in the 100 gallon pfaudler and the "base" terpolymer contained 1.44 mole% PMS and 0.68 mole% Br-PMS. The experiments were carried out in a two-phase, water/organic system under nitrogen in a 2 liter jacketed flask. The organic solvent used consisted of a 50:50 (wt:wt) mixture of tetrahydrofuran and toluene.

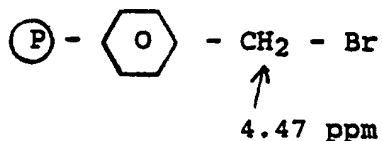
A 5% "base" terpolymer solution was prepared by dissolving 60 grams of "base" terpolymer in 1200 grams solvent. The dissolution takes a number of hours and was always done overnight. The aqueous phase consisted of Bu_4NOH (phase transfer catalyst), NaOH and CH_3COOH to a total volume of 60 ml. The amounts of these components is given in Table 1. After the addition of the aqueous solution, the reactor was heated to reflux at 74.5°C . (Note: It takes

- 142 -

1 hour to reach reflux temperature.) The refluxing continued for the next 6 to 8 hours. The samples were withdrawn from the reactor every hour and given three 1% aqueous HCl and three 10% aqueous isopropanol washes. The samples were then recovered in isopropanol. Antioxidant was added by soaking the polymer in a 0.5% (wt) solution of butylated hydroxytoluene (2,6-ditertbutyl-4-methylphenol) in isopropyl alcohol. They were then dried in a vacuum oven at 65°C for 48 hours.

Results of a number of experiments are tabulated in Table 1 and show that any desired ratio of the three functionalities can be achieved by proper selection of reaction conditions. With excess acid as in runs 13968-89, 13968-102, and 13968-106 only ester functionality is achieved by the nucleophilic substitution reaction. The rate of ester formation by replacement of the benzylic bromines for reaction 13968-102 is plotted in Figure 3. With excess base present, the ester is hydrolyzed to hydroxy by the sequential reaction so a mixed functionality product can be produced. The rate at which the various functionalities form and disappear for reaction 13968-70 is plotted in Figure 4.

In each case, proton NMR spectra was used to quantify the amounts of pendant functionality present:



- 143 -

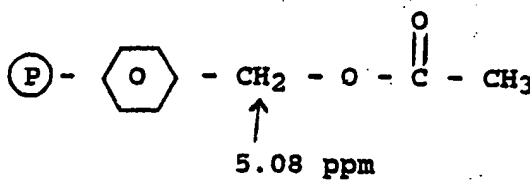


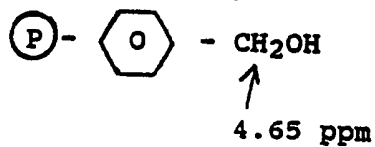
TABLE 1

Reaction Number	Poly.g	Solvent and Weight (g)	H ₂ O, ml	Bu ₄ NOH (g) and Bu ₄ NOH/Br	NaOH (g) and NaOH/Br	CH ₃ COOH (g) and CH ₃ COOH/Br	Run Temp. °C	Run Time (Hours)	Product Analysis, NMR-Mole%
13968-70	40.75 (14470-68-4D)	Toluene- 400.0 THF - 401.7	40	1.62 .50 (Br)	50% NaOH 40.83 67 (Br)	6.05 13 (Br)	74.5(R)	7.0	BrPMS-.04 OHPMS-.59 Ester-.05
13968-72	60.37 (14470-68-4D)	Toluene- 602.5 THF - 602.2	60	3.64 .75 (Br)	50% NaOH 60.22 100 (Br)	9.00 20 (Br)	74.5(R)	6.5	BrPMS-.03 OHPMS-.65 Ester-.01
13968-74	59.37 (14470-68-4D)	Toluene- 636.5 THF - 605.5	60	3.62 .75 (Br)	50% NaOH 36.83 60 (Br)	9.00 20 (Br)	74.5(R)	6.0	BrPMS-.06 OHPMS-.60 Ester-.05
13968-76	59.47 (14470-68-4D)	Toluene- 654.3 THF - 606.2	60	3.61 .75 (Br)	50% NaOH 24.20 40 (Br)	9.05 20 (Br)	74.5(R)	8.0	BrPMS-.04 OHPMS-.47 Ester-.16
13968-78	60.35 (14470-68-4D)	Toluene- 597.0 THF - 599.9	50.6	3.69 .75 (Br)	50% NaOH 14.43 24 (Br)	9.02 20 (Br)	74.5(R)	13.0	BrPMS-.00 OHPMS-.34 Ester-.35
13968-83	59.61 (14470-68-4D)	Toluene- 598.0 THF - 600.0	52	3.62 .75 (Br)	50% NaOH 11.99 20 (Br)	9.00 20 (Br)	74.5(R)	13.0	BrPMS-.06 OHPMS-.00 Ester-.60
13968-89	60.68 (14470-68-4D)	Toluene- 602.0 THF - 607.0	53	3.62 .75 (Br)	12.21 20 (Br)	18.15 40 (Br)	74.5(R)	13.0	BrPMS-.21 OHPMS-.00 Ester-.47

TABLE 1

Reaction Number	Poly.g	Solvent and Weight (g)	H ₂ O, ml	Bu ₄ NOH (g) and Bu ₄ NOH/Br	NaOH (g) and NaOH/Br	CH ₃ COOH (g) and CH ₃ COOH/Br	Run Temp. °C	Run Time (Hours)	Product Analysis, NMR-Mole%
13968-92	60.07 (14470-68-4D)	Toluene-1201.0	44	2.60 .50 (Br)	29.96 50 (Br)	9.00 20 (Br)	94.5	7.0	BrPMS-.00 OHPMS-.56 Ester-.07
13968-102	60.00 (14470-68-4D)	Toluene- 600.7 THF - 601.3	55	3.59 .75 (Br)	12.01 20 (Br)	9.33 21 (Br)	73.5(R)	6.0	BrPMS-.30 OHPMS-.00 Ester-.44
13968-106	60.00 (14470-68-4D)	Toluene- 600.0 THF - 600.4	60	3.61 .75 (Br)	6.01 20 (Br)	9.33 21 (Br)	74.5	14.0	BrPMS-.12 OHPMS-.00 Ester-.61
13968-108	60.00 (14470-68-4D)	Toluene-1200.0	60	3.70 .75 (Br)	29.00 100 (Br)	8.97 20 (Br)	74.5	6.0	BrPMS-.00 OHPMS-.55 Ester-.04
13968-125	61.11 (14470-68-4D)	Heptane-1200.0	60	3.61 .75 (Br)	6.00 20 (Br)	9.08 20 (Br)	82.0	8.0	No RXN
13968-147	200 (14470-42-6D)	Toluene-1800.0	180	10.41 .75 (Br)	101.69 116 (Br)	30.04 23 (Br)	74.0	5.0	BrPMS-.00 OHPMS-.46 Ester-.03
13968-148	200 (15271-1-4D)	Toluene-1800.0	200	10.50 .75 (Br)	50% NaOH 40.13 23 (Br)	30.37 23 (Br)	75.5	3.5	BrPMS-.34 OHPMS-.00 Ester-.12

- 146 -



This sequential esterification, hydrolysis reaction route is thus capable of yielding a range of very useful pendant functionalized polymers.

Example 8

Preparation of Pendant Functionalized
Isobutylene/Paramethyl Styrene Copolymers
Containing Mercaptan Groups

In this example, pendant mercaptan functionality was attached to a random isobutylene/paramethyl styrene/para-bromomethylstyrene "base" terpolymer by nucleophilic substitution using NaSH as the nucleophilic reagent. This reaction must be conducted in a two-phase system using phase transfer catalysis with the NaSH nucleophilic reagent dissolved in the aqueous phase and the "base" terpolymer in the organic phase. Sequential reactions leading to cross-linking are difficult to control and the product oxidatively cross-links to form disulfide linkages readily on exposure to air at elevated temperatures so it is not a very stable pendant. Nevertheless, the active product mercaptan groups are useful in vulcanization and co-vulcanization and in self-cross-linking systems of various types.

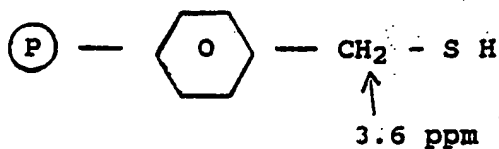
The "base" terpolymer used in this example was a very low molecular weight isobutylene/paramethyl styrene/para-bromomethylstyrene terpolymer produced in the laboratory by light initiated radical bromination of a pilot plant produced random isobutylene/paramethyl styrene copolymer. It had a viscosity average molecular weight of 10,000 and contained 1.1 mole% paramethyl styrene 1.6 mole % para-bromomethylstyrene and 97.3 mole% isobutylene.

- 148 -

In the nucleophilic substitution reaction, 250 g of the "base" terpolymer was dissolved in 1000 g hexane in a 2 l resin flask under nitrogen to form a 20% solution by weight. Then an aqueous solution consisting of 11.0 g NaSH, 1.0 g tetrabutyl ammonium bromide and 25 g of distilled water was poured in with stirring to form an emulsion which was heated to 65°C and stirred hot for 11 hours before being allowed to cool. All materials were handled and charged under nitrogen and the reaction was conducted with continuous nitrogen bubbling through a fritted glass bubbler to rigorously exclude oxygen. The charge was about 1.4 mole% of the NaSH nucleophilic reagent per mole of benzylic bromine. After cooling the solution was washed several times with dilute NaOH at ice water temperature to remove salts and unreacted NaSH and then given several cold water washes before being precipitated in methanol. The polymer was stabilized with 0.1 wt% BHT and 0.1 wt% Methyl Tuods and then vacuum oven dried at 70°C to recover a soft, sticky, light tannish pendant mercaptan functionalized polymer. All washing, recovery and drying was done in a nitrogen atmosphere to prevent oxidative cross-linking. Despite these precautions the recovered polymer had a viscosity average molecular weight of 20,700 showing that some cross-linking did occur, but the product was still completely soluble. The product contained 0.8 wt% sulfur and contained 1.5 mole% pendant mercaptan functionality by NMR analyses. It also contained 1.0 wt% residual bromine but less than oil mole % residual benzylic bromide by analyses.

Proton NMR spectra was used to quantify the amount of pendant functionality present.

- 149 -



This example shows that under the proper conditions pendant mercaptan functionality can be attached to the "base" terpolymer of this invention without producing a gelled product.

In total these examples have shown that any of the nucleophilic substitution reactions described and claimed in this invention can be accomplished by carefully observing the key requirements taught herein to produce the versatile and useful soluble, backbone saturated pendant functionalized polymers claimed.

- 150 -

CLAIMS:

1. A functionalized polymer of an isolefin having about 4 to about 7 carbon atoms and a para-alkylstyrene, wherein at least one type of a functional group is attached to the para-alkyl group of the para-alkylstyrene, said polymer having a substantially homogeneous compositional distribution.

2. The functionalized polymer of claim 1 wherein said copolymer has a number average molecular weight of at least about 25,000.

3. The functionalized polymer of claim 1 wherein said polymer has a number average molecular weight of between about 500 and 25,000.

4. The functionalized polymer of claim 1 wherein said polymer has a ratio of \bar{M}_w/\bar{M}_n of less than about 6.

5. The functionalized polymer of claim 1 wherein said polymer has a ratio of \bar{M}_w/\bar{M}_n of less than about 2.5.

6. The functionalized polymer of claim 1 wherein said polymer has a ratio of \bar{M}_w/\bar{M}_n of less than about 2.

7. The functionalized polymer of claim 1 wherein at least about 95 wt.% of said polymer has a para-alkylstyrene content within about 10 wt.% of the average para-alkylstyrene content for said polymer.

- 151 -

8. The functionalized polymer of claim 7 wherein the normalized differential refractive index and ultraviolet curves obtained by gel permeation chromatography for said polymer are essentially superimposable.

9. The functionalized polymer of claim 1 wherein said isoolefin comprises isobutylene and said para-alkylstyrene comprises para-methylstyrene.

10. The functionalized polymer of claim 9 wherein said polymer has a number average molecular weight of greater than about 25,000.

11. The functionalized polymer of claim 10 wherein said polymer has a ratio of M_w/M_n of less than about 6.

12. The functionalized polymer of claim 11 wherein said polymer has a ratio of M_w/M_n of less than about 2.5.

13. The functionalized polymer of claim 1 wherein said isoolefin and said para-alkylstyrene are present in said polymer in amounts such that said isoolefin comprises from about 10 to 99.5 wt.% of said polymer and said para-alkylstyrene comprises from about 0.5 to 90 wt.% of said polymer.

14. The functionalized polymer of claim 1 wherein said isoolefin and said para-alkylstyrene are present in said polymer in amounts such that said isoolefin comprises from about 80 to 99 wt.% of said

- 152 -

polymer and said para-alkylstyrene comprises from about 0.5 to 20 wt.% of said polymer.

15. The functionalized polymer of claim 13 or 14 wherein said isoolefin comprises isobutylene and said para-alkylstyrene comprises para-methylstyrene.

16. The functionalized polymer of claim 15 wherein said polymer has a number average molecular weight of greater than about 50,000.

17. The functionalized polymer of claim 16 wherein said polymer has a number average molecular weight of greater than about 100,000.

18. The functionalized polymer consisting essentially of the direct reaction product of isoolefin having from 4 to 7 carbon atoms and para-alkylstyrene, said polymer having a number average molecular weight of greater than about 25,000.

19. The functionalized polymer of claim 18 wherein said polymer has a ratio of \bar{M}_w/\bar{M}_n of less than about 6.

20. The functionalized polymer of claim 19 wherein said polymer has a ratio of \bar{M}_w/\bar{M}_n of less than about 2.5.

21. The functionalized polymer of claim 20 wherein said polymer has a ratio of \bar{M}_w/\bar{M}_n of less than about 2.0.

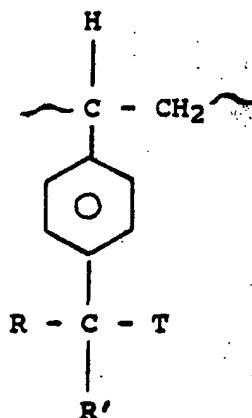
- 153 -

22. The functionalized polymer of claim 18 wherein said polymer has a number average molecular weight of greater than about 50,000.

23. The functionalized polymer of claim 22 wherein said polymer has a number average molecular weight of greater than about 100,000.

24. The functionalized polymer of claim 18 wherein said isocolefin comprises isobutylene and said para-alkylstyrene comprises para-methylstyrene.

25. The functionalized polymer of claim 18 wherein said polymer includes said para-alkylstyrene as



wherein R and R' are independently selected from the group consisting of hydrogen, alkyl, and the primary and secondary alkyl halides, wherein T is a mixture of a halogen and at least one functional group containing oxygen, sulfur, silicon, nitrogen carbon, phosphorous, and/or metals including sodium, potassium, lithium, and magnesium.

- 154 -

26. The functionalized polymer of claim 25, wherein Y is selected from the group consisting of alkoxide, phenoxide and carboxylates.

27. The functionalized polymer of claim 25, wherein Y is selected from the group consisting of thiolates, thiophenolates, thioethers, thiocarboxylates, dithiocarboxylates, thioureas, dithiocarbamates, xanthates and thiocyanates.

28. The functionalized polymer of claim 25, wherein Y is selected from the group consisting of silanes halosilanes, malonates, cyanides, and CR'₃, wherein R' is an alkyl group of about 1 to about 18 carbon atoms.

29. The functionalized polymer of claim 25, wherein Y is selected from the group consisting of amides, amines, carbazoles, phthalimides, pyridine, maleimide and cyanates.

30. The functionalized polymer of claim 25, wherein Y is phosphines.

31. The functionalized polymer of claim 25 wherein R and R' are independently selected from the group consisting of hydrogen, C₁ to C₅ alkyl and the C₁ to C₅ primary and secondary alkyl halides.

32. The functionalized polymer of claim 18 wherein said isoolefin and said para-alkylstyrene are present in said polymer in amounts such that said isoolefin comprises from about 80 to 99.5 wt.% of said

- 155 -

polymer and said para-alkylstyrene comprises from about 0.5 to 20 wt.% of said polymer.

33. The functionalized polymer of claim 18 wherein said isocolefin and said para-alkylstyrene are present in said polymer in amounts such that said isocolefin comprises from about 10 to 99.5 wt.% of said polymer and said para-alkylstyrene comprises from about 0.5 to 90 wt.% of said polymer.

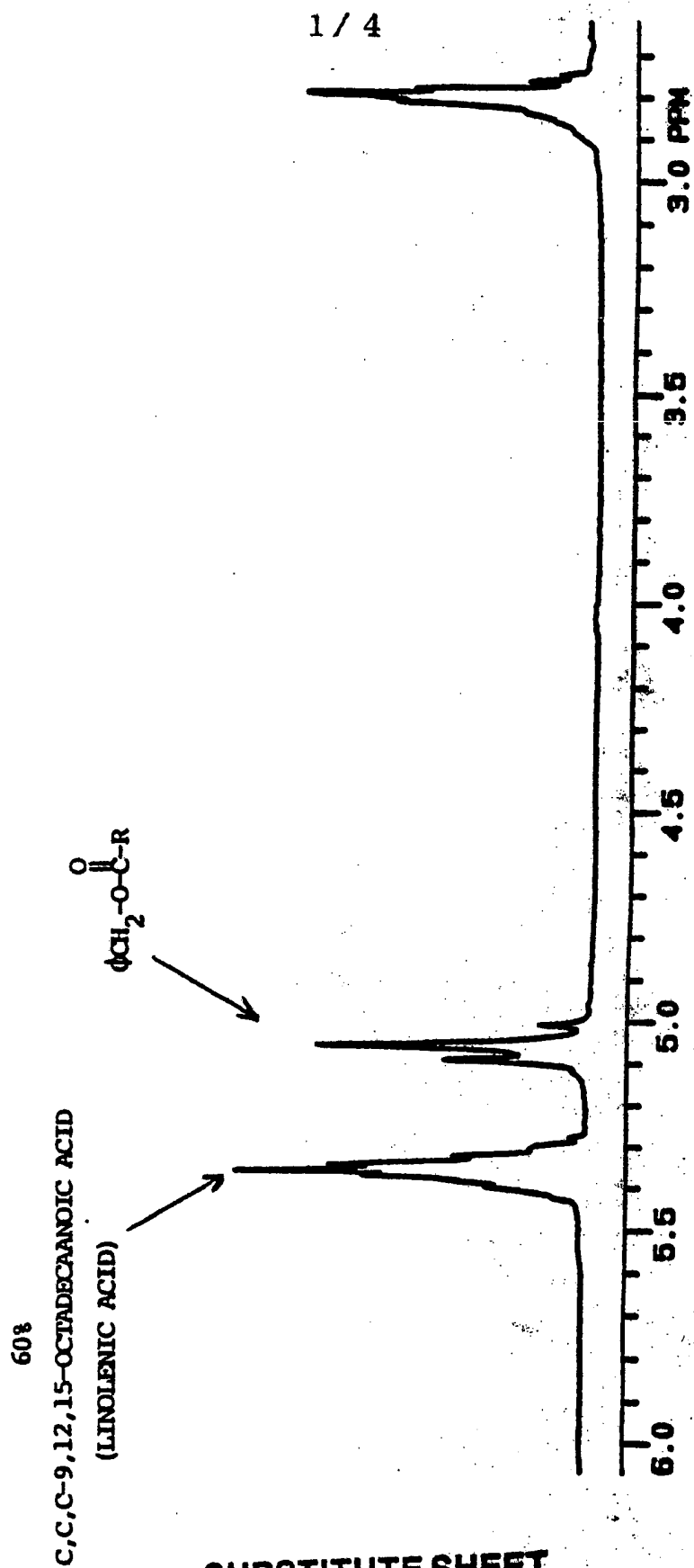
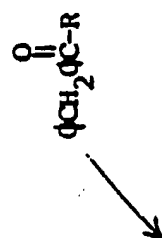


FIG. 1

SUBSTITUTE SHEET

2 / 4



80%

C,t,t-9,11,13-OCTADECANOIC ACID
(ELEOSTEARIC ACID)

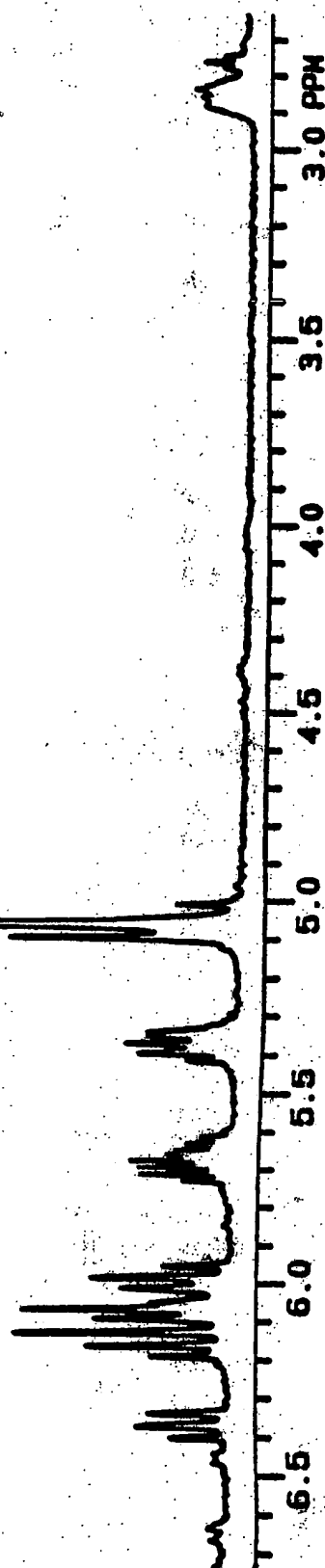


FIG. 2

SUBSTITUTE SHEET

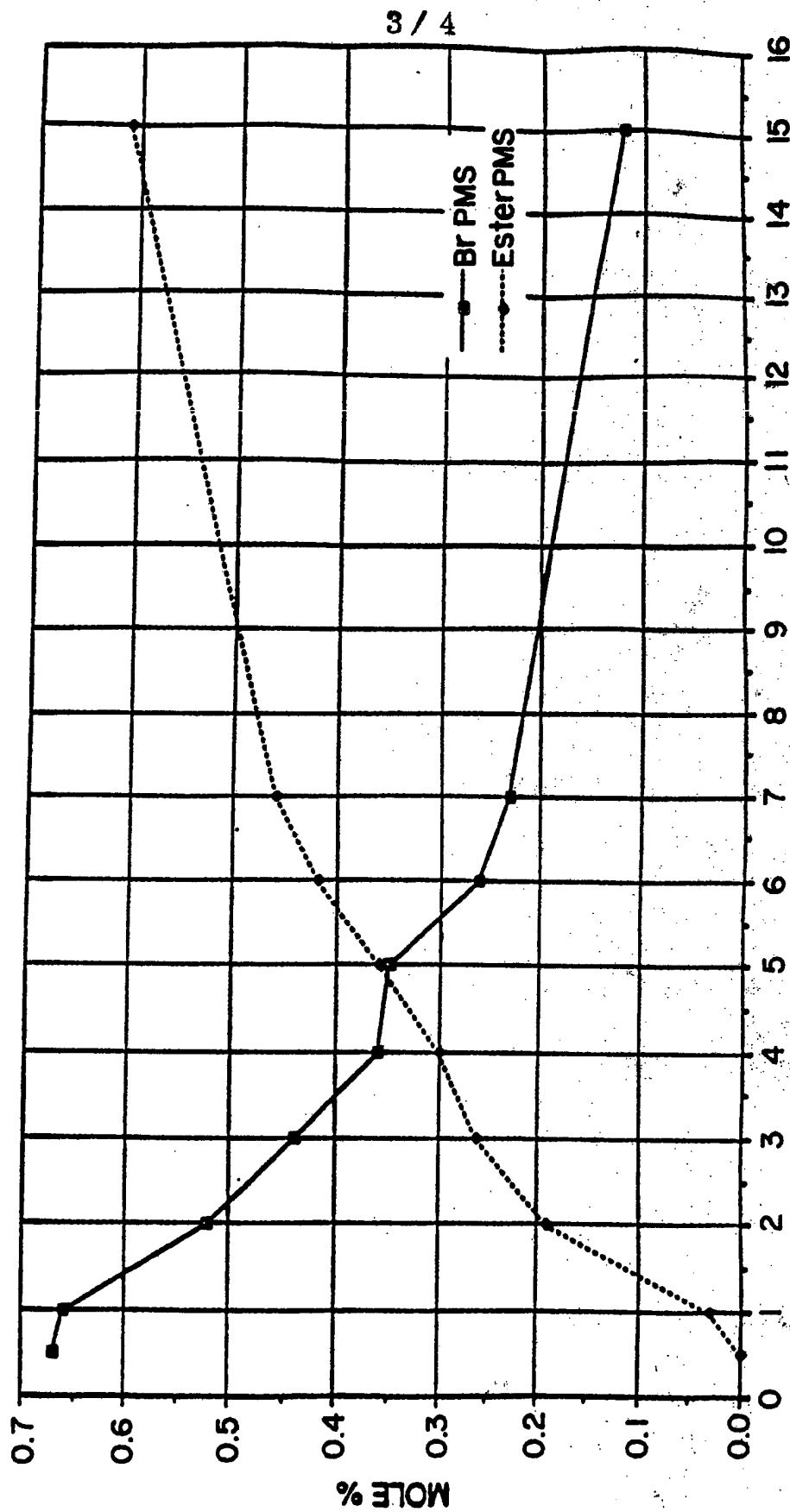


FIG. 3

SUBSTITUTE SHEET

4/ 4

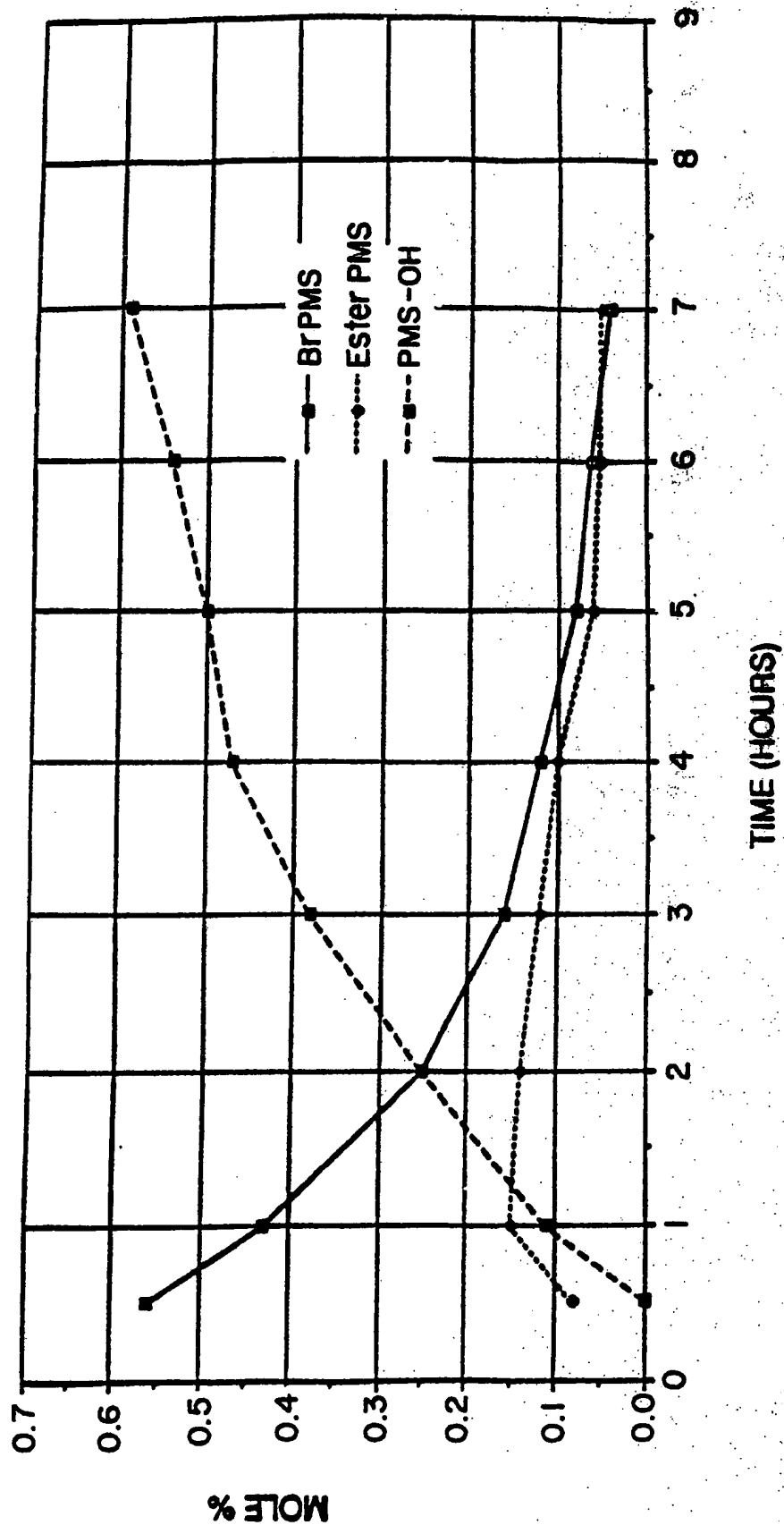


FIG. 4

INTERNATIONAL SEARCH REPORT

International Application No. **PCT/US 89/05315**

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: C 08 F 8/00, C 08 F 8/42, C 08 F 210/10, C 08 F 210/14 // (C 08 F 210/10, 212:12). (C 08 F 210/14, 212:12)														
II. FIELDS SEARCHED <div style="text-align: center; border: 1px solid black; padding: 2px;">Minimum Documentation Searched⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 25%; border: 1px solid black; padding: 2px;">Classification System</th> <th style="border: 1px solid black; padding: 2px;">Classification Symbols</th> </tr> <tr> <td style="border: 1px solid black; padding: 5px; height: 40px; vertical-align: top;">IPC5</td> <td style="border: 1px solid black; padding: 5px; vertical-align: top;">C 08 F</td> </tr> </table> <div style="border: 1px solid black; padding: 2px; margin-top: 5px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched⁸</div>			Classification System	Classification Symbols	IPC5	C 08 F								
Classification System	Classification Symbols													
IPC5	C 08 F													
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%; padding: 2px;">Category¹⁰</th> <th style="width: 60%; padding: 2px;">Citation of Document,¹¹ with indication, where appropriate, of the relevant passages¹²</th> <th style="width: 30%; padding: 2px;">Relevant to Claim No.¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">E</td> <td style="padding: 5px;">EP, A2, 0344021 (EXXON CHEMICAL PATENTS INC.) 29 November 1989, see the whole document --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-24, 32-33</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">EP, A2, 0243124 (TOA NENRYO KOGYO KABUSHIKI KAISHA) 28 October 1987, see abstract; claims 1-16 --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">EP, A2, 0189672 (TOA NENRYO KOGYO KABUSHIKI KAISHA) 6 August 1986, see page 3, line 15 - line 18; abstract; claims 1-21 --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1, 2, 18, 25, 32, 33</td> </tr> </tbody> </table>			Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	E	EP, A2, 0344021 (EXXON CHEMICAL PATENTS INC.) 29 November 1989, see the whole document --	1-24, 32-33	A	EP, A2, 0243124 (TOA NENRYO KOGYO KABUSHIKI KAISHA) 28 October 1987, see abstract; claims 1-16 --	1	A	EP, A2, 0189672 (TOA NENRYO KOGYO KABUSHIKI KAISHA) 6 August 1986, see page 3, line 15 - line 18; abstract; claims 1-21 --	1, 2, 18, 25, 32, 33
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³												
E	EP, A2, 0344021 (EXXON CHEMICAL PATENTS INC.) 29 November 1989, see the whole document --	1-24, 32-33												
A	EP, A2, 0243124 (TOA NENRYO KOGYO KABUSHIKI KAISHA) 28 October 1987, see abstract; claims 1-16 --	1												
A	EP, A2, 0189672 (TOA NENRYO KOGYO KABUSHIKI KAISHA) 6 August 1986, see page 3, line 15 - line 18; abstract; claims 1-21 --	1, 2, 18, 25, 32, 33												
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p> </div> </div>														
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border: 1px solid black; padding: 5px;"> Date of the Actual Completion of the International Search 1st June 1990 </td> <td style="width: 50%; border: 1px solid black; padding: 5px;"> Date of Mailing of this International Search Report 13 JUN 1990 </td> </tr> <tr> <td style="border: 1px solid black; padding: 5px;"> International Searching Authority EUROPEAN PATENT OFFICE </td> <td style="border: 1px solid black; padding: 5px;"> Signature of Authorized Officer Mme N. KUIPER </td> </tr> </table>			Date of the Actual Completion of the International Search 1st June 1990	Date of Mailing of this International Search Report 13 JUN 1990	International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer Mme N. KUIPER								
Date of the Actual Completion of the International Search 1st June 1990	Date of Mailing of this International Search Report 13 JUN 1990													
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer Mme N. KUIPER													

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	<p>Dialog Information Services, File 351, World Patent Index 81-90, Dialog accession no. 88-026337/04, Toa Nenryo Kogyo KK: "Prodn. of substit.-contg. styrene polymers - from polymers contg. p-methylstyrene skeleton, organo lithium opds. and lithium extracting agents", JP 62288606, A, 871215, 8804 (Basic)</p> <p>--</p> <p>-----</p>	1

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. PCT/US 89/05315**

SA 32709

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 07/05/90
The European Patent office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A2- 0344021	29/11/89	AU-D- 3521989	30/11/89
EP-A2- 0243124	28/10/87	JP-A- 62246905 US-A- 4704438	28/10/87 03/11/87
EP-A2- 0189672	06/08/86	JP-A- 61151203	09/07/86

For more details about this annex : see Official Journal of the European patent Office, No. 12/82

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)